

VIBRATIONAL STUDIES OF SOLID INORGANIC AND COORDINATION COMPLEXES AT HIGH PRESSURES *

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A. INTRODUCTION

The earliest high-pressure studies were made by Amagat [1], but the important and fundamental studies on high pressure were conducted by Bridgman [2-16] who has been called the father of high-pressure chemistry. Bridgman

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was able to attain pressures to 10^5 atm. His work still finds extensive use today, and his compressibility data as a function of pressure for common liquids was a classical achievement.

There are several books and reviews [3,17–26] on high pressure, some of which cover the history of high pressure comprehensively. It is not intended in this review article to dwell on the history of high pressure to any large degree for fear of being redundant with already published material.

The general effects of pressure on matter have been discussed by Sinn [26].

It is the aim of this review to discuss the effects of pressure to 150 kbar on the vibrational transitions occurring in solid materials such as inorganic compounds and coordination complexes. The magnitudes of these effects are measured by IR and Raman scattering methods. The review restricts itself chiefly with the versatile diamond anvil cell. Electronic transitions have been discussed by Drickamer and Frank [27].

(i) Units of pressure

A brief discussion on the units of pressure is necessary at this point. The international standard (SI) unit of pressure is the Pascal or Newton per square meter. The interrelationships between various units in use today and the SI units are given as follows

$$1 \text{ bar} = 10^5 \text{ N m}^{-2} \text{ (or Pascal)} = 10^6 \text{ dyne cm}^{-2} = 0.9869 \text{ atm} = 1.0197 \text{ kg cm}^{-2}$$

$$1 \text{ atm} = 1.01325 \times 10^6 \text{ dyne cm}^{-2}$$

We will use kbar in this discussion, which corresponds to 10^3 bar, and at extremely high pressures, Mbar, where $1 \text{ Mbar} = 10^3 \text{ kbar}$.

To provide the newcomer with an idea of the magnitude of some of these pressure values, Table 1 has been compiled.

TABLE 1
Naturally occurring pressures [26]

Pressure (kbar)	Site of occurrence
1	Deepest part of ocean — Marianas trench
10	Crust—mantle interface — Mohorovicic discontinuity
1.37×10^3	Mantle—core interface — Wichert-Gutenberg discontinuity
3.64×10^3	Center of earth
1×10^8	Center of sun
10^{10} — 10^{14}	White dwarf star
10^{17} — 10^{21}	Neutron stars

B. INSTRUMENTATION FOR OPTICAL MEASUREMENTS AT HIGH PRESSURES [28]

The instrumentation necessary to make spectroscopic measurements at non ambient pressures includes an optical high pressure cell, a spectrophotometer, and the interface or optical link of the cell with the spectrophotometer. The optical link of the pressure cell to an IR spectrophotometer necessitates the use of a beam condenser, and to an interferometer a light-pipe or a beam condenser may be necessary. Very important considerations of this instrumentation are the windows used in the optical high pressure cell. The properties of the windows are of prime importance since they must be transparent to the electromagnetic radiation of interest and must be of sufficient strength to withstand high pressures. Ancillary equipment for some systems may include pressure-transmitting and pressure-measuring devices.

(i) Optical high pressure cells

The high pressure cells which can be used for optical purposes may be of three main types: (1) shock wave cell; (2) piston-cylinder cell; and (3) opposed anvil cell. Table 2 summarizes advantages and disadvantages of the three types of cells.

(1) Shock wave cell

The shock wave cell utilizes high explosives to obtain pressure and will give the highest pressures of any cell discussed in this paper [29]. However, the pressures are of short duration and may be destructive to the sample and optical equipment; moreover making the optical link to a spectrophotometer is difficult. Since the effects of pressure are of short duration (10^{-5} s) fast-scanning spectrophotometers are necessary. Except in specialized cases where extreme pressures are necessary to demonstrate some phenomenon, the shock wave cell and technique are less practical than the piston-cylinder or the opposed anvil cell. Many of the physical measurements that are possible with the latter two cells on in situ samples are not possible with shock-waves.

(2) Piston-cylinder cell

The piston-cylinder type cell or variations thereof have made notable contributions and can be used in an extended region of the electromagnetic spectrum from the UV region to the IR. The piston-cylinder cell has been used primarily for solids, although it has been adapted for use with liquids or solutions as well.

The best known cell of this type is the supported taper Drickamer cell, which was developed by Drickamer and his students [30–33], and is a cross between an anvil and a piston-cylinder apparatus. Several variations of this cell have now been made. Tables 3 and 4 summarize details of the pressure

TABLE 2
Types of optical high pressure cells

Type of cell	Pressure (kbar)	Advantages	Disadvantages
Shock wave	>>1000	1. Highest obtainable pressures	1. Pressure exerted over short time 2. May be destructive to optical equipment and sample 3. High explosives needed to obtain shock wave
Piston and cylinder ^a	180	1. Largest specimen volume 2. Gives more nearly hydrostatic pressures 3. Can be used for liquids or solutions	1. Insufficient optical clarity to permit microscopic observation or photography of sample 2. Specimen may interact with salt matrix 3. Difficult to use
Opposed anvils (diamonds)	1700	1. Only micro quantities of material necessary. 2. Compact — can be used with spectrophotometers and microscope easily 3. Can use for liquids or solutions 4. No matrix interference	1. Pressure gradient exists in cell 2. Absorption of diamonds may be troublesome 3. Cannot use large specimen of solids

^a Or modifications thereof.

cells that are in use for optical studies of solids and liquids or solutions.

The piston-cylinder cell is considered to give essentially hydrostatic pressures, an important consideration in pressure studies. The Drickamer cell has two versions, one capable of providing pressures up to 60 kbar and the other to 200 kbar. Figure 1 shows the design of one of these cells. The pressure is exerted perpendicular to the light path. Sodium chloride serves as the spectroscopic window and the pressure-transmitting fluid.

The sample is loaded into the center of a small disc of NaCl. Although the cell accommodates the largest possible sample specimen for pressure measurements, the sample is surrounded by a salt matrix. If one wishes to study pressure effects on ionic solids, this could present a problem. Additionally, the hygroscopic nature of the salt matrix is detrimental. Other materials besides NaCl may be substituted for the center disc. This has the disadvantage in that it would shorten the life of the NaCl windows, and the matrix problem would always exist.

TABLE 3

Piston-cylinder cell (solids)^a

Pressure limits (kbar)	Optical instrument	Windows	Wavelength range (μm)	Remarks	Ref.
160	Beckman DU (0.25–10 μm), Perkin-Elmer single beam, double prism instrument in IR	NaCl	UV, Visible NIR, MIR to 10	Sapphire, CaF ₂ windows have also been used; 80–450 K	30–33
30	Beckman	Quartz, sapphire	0.36–0.40		36
30 ^c	IKS-12	Diamond	5–6		37
55	RIIC, Grubb-Parsons Cube interferometer	Sapphire, diamonds (type II) MgO, fused silica, Irtran	1–1000	77–500 K ^{64,65}	35
10–20 ^{c,d}	Perkin-Elmer Coderg	Sapphire Diamond	1–5 100–1000	2–300 K	Vu ^b
9	RIIC 720FS interferometer and <i>f</i> -2 single pass grating instrument of Ebert type	Quartz	90–500	For FIR, hydrostatic gas pressure cell	38 ^b
50	PE 421, 400, JACO	NaCl		77–500 K	46 ^b

^a Abbreviations: NIR, near infrared; MIR, mid-infrared; FIR, far infrared. ^b Personal communication. ^c Can be used for liquids as well.^d Can be used for gases as well.

TABLE 4
Piston-cylinder cells (liquids or solution)

Pressure limits (kbar)	Optical instrument	Windows	Wavelength range (μm)	Remarks	Ref.
200 ^a	Perkin-Elmer model 521	KBr or NaCl	5-6	Used to study carbonyl reactions in metal carbonyls	39
40	Beckman DK-2	Sapphire	0.2-0.33	Solutions of inorganic salts in H ₂ O	40
10-12	Perkin-Elmer model 112	Sapphire	0.2-5	Studied ν_{OH} band in butanol solutions of CS ₂	41
1.5	Beckman IR-5A ^b	Irtran 1 or 2	~6	Study of C \equiv C vibration	42
10					
12 ^c	(?)	Sapphire	3	Studies of H ₂ O	43
1	(?)	Sapphire	(?)	Cell claimed to be suitable for use to 6 kbar	44

^a Can be used to 373 K. ^b With grating monochromator. ^c Similar to Drickamer cell in Table 3.

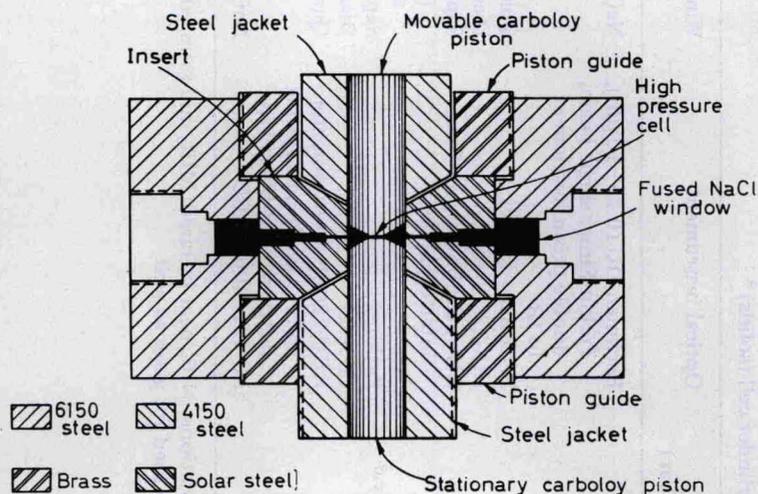


Fig. 1. Drickamer cell used for high pressure optical measurements [30-33]. (Figure reproduced through the courtesy of the authors and John Wiley and Sons, Inc., New York.)

The use of this cell requires a high degree of expertise and further requires high precision machine shop facilities to construct it. The cell has been used for pressure applications of 180 kbar at 773 K [34] and 55 kbar at 77 K [35]. The cell has been modified to be used for liquids or solutions [41,43]. The Drickamer cell or modifications thereof have also been used for Raman measurements at high pressures [45,46]. This application will be discussed in a later section. A Drickamer-type apparatus for pressures to 400 kbar has been reported [47].

(3) Anvil-type cell

Perhaps the most versatile pressure cell that has been used for optical studies has been the diamond anvil cell (DAC), as developed by Weir and associates [48]. Figure 2 shows the details of this cell. The diamonds serve as the pressure transmitting material as well as the windows. Pressures close to 100 kbar, depending on the size of the diamonds, are routinely reached. However, the DAC has been used with pressure as high as 300 kbar [49], and conceivably smaller diamonds could generate even higher pressures. The cell can be used for solutions or liquids, although a gasket is necessary for this application. Figure 3 illustrates a gasketing technique used with liquids [50]. The

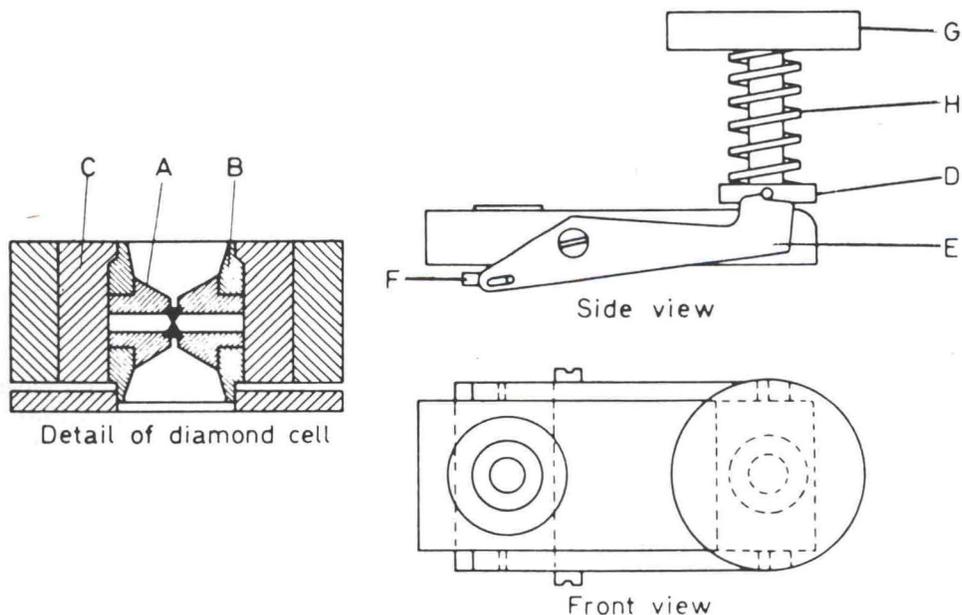


Fig. 2. Diamond anvil high pressure optical cell. A and B, parts of pistons; C, hardened steel insert; D, pressure plate; E, lever; G, screw; H, calibrated spring. (Figure reproduced through the courtesy of the authors and Applied Spectroscopy.)

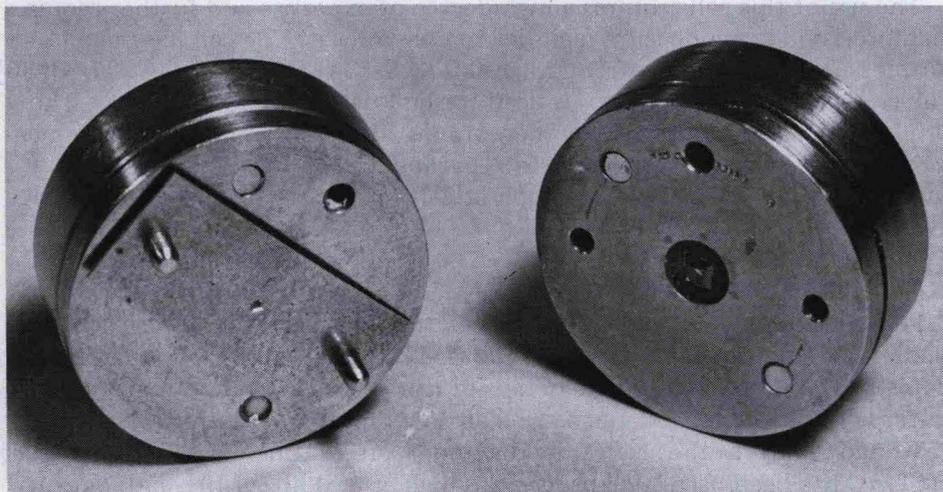


Fig. 3. A gasket technique with DAC [50]. (Figure reproduced through the courtesy of the authors and Applied Spectroscopy.)

DAC has also been used at temperatures of ca. 3000 K [51] and cooled down to liquid nitrogen temperatures [52].

Recently improved versions of the DAC were developed [53,54], and Fig. 4 illustrates the details of the modifications used by Adams and Payne. Pressure in this cell is applied through a small hydraulic ram instead of the calibrated screw of the original version. The other improved version of the DAC is the Waspaloy cell [54]. Figure 5 shows the essential parts of the design. The diamond alignment is improved from the original design. One diamond is mounted in a hemisphere, while the other diamond is mounted on a plate which is translationally positioned for axial alignment by screw adjustments. A loose fitting heating coil is placed in the cell. The cell can be used with gaskets for hydrostatic pressure to 100 kbar, and has been used to 973 K and 200 kbar pressure.

An ultrahigh pressure diamond cell has now been developed [55], and megabar pressures can be generated. The cell is made of hardened (RWC-55) 4340 alloy steel. For high temperature studies the cell can be made from Inconel. Mao and Bell [56] have described an ultrahigh-pressure diamond cell, which they claim to have used to 1.7 Mbar [57]. These new ultrahigh pressure cells now make experiments simulating geochemical reactions in the mantle of the earth possible.

One shortcoming of the DAC is the lack of hydrostatic pressure across the diamond faces. This pressure gradient, which may demonstrate pressures 1.5 times greater at the center than the edges [58], may not be entirely disadvantageous. However, with the use of a gasket and a pressure transmitting fluid the

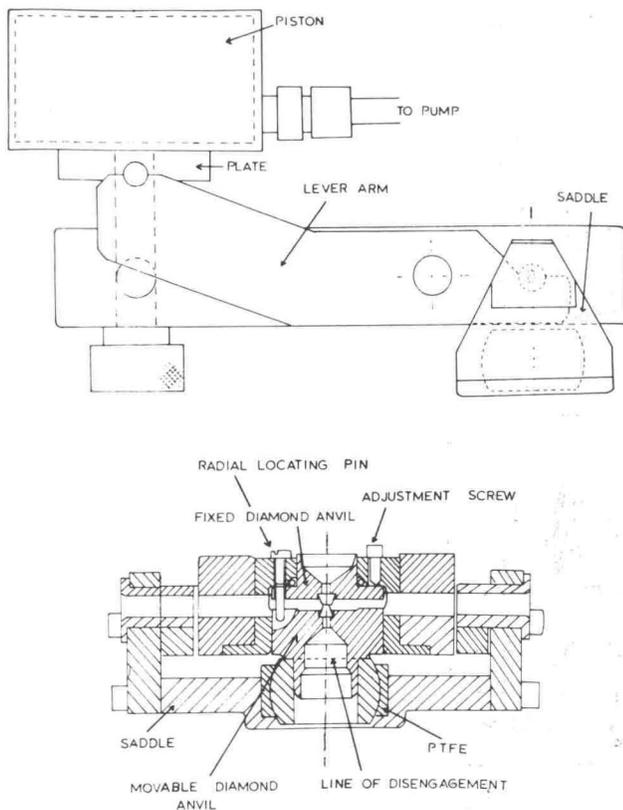


Fig. 4. Modified DAC cell [53]. (Figure reproduced through the courtesy of the authors and Applied Spectroscopy.)

the problem of non-hydrostatic pressure can be circumvented. Phase changes may be readily identified in the DAC, using a microscope, by the change in color occurring and the sharp demarcation between phases. Color changes alone, particularly in coordination compounds, do not necessarily indicate a phase change. A primary requisite is the appearance of the Becke line of demarcation. In colorless materials, the phase changes may be identified by the Becke line, which demarcates the phases. The DAC is compact and can be readily used with a microscope. All loadings of solid materials into the DAC should be monitored microscopically to ensure a proper distribution in the cell. This procedure prevents any diamond-diamond contact, which could cause chipping or gouging of the diamonds. Additionally, such monitoring can alert the experimenter to any phase change or other phenomena occurring.

The DAC has also been used for Raman work at high pressures, and this instrumentation will be discussed later [53,59-61].

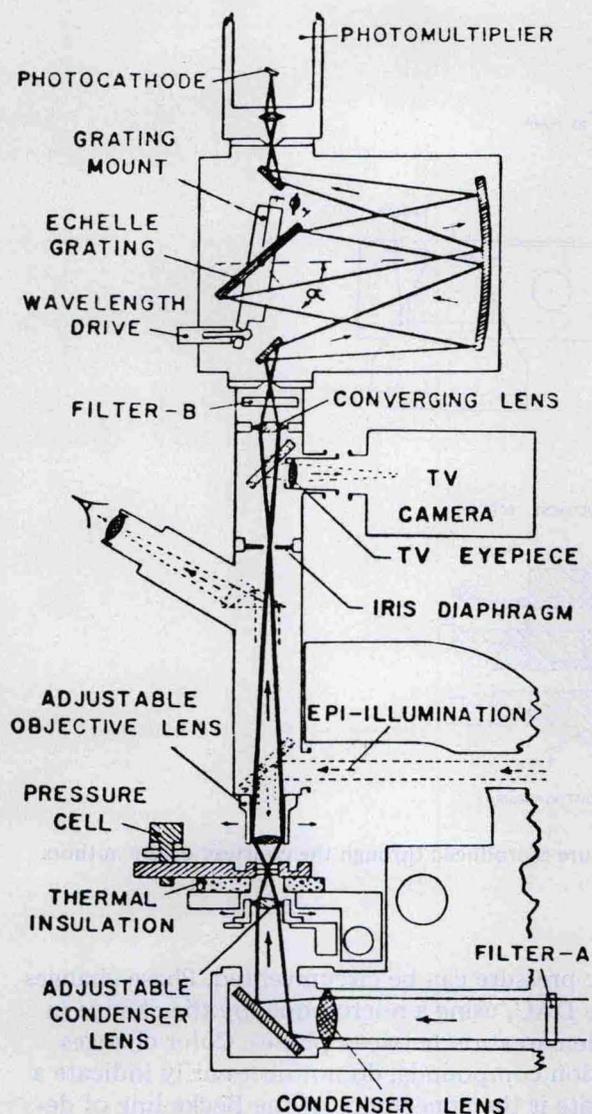


Fig. 5. Details of the Waspaloy pressure cell [54]. (Figure reproduced through the courtesy of the authors and Review of Scientific Instruments.)

Table 5 summarizes the details of some of the anvil cells that are in use for optical studies.

(ii) *Optical link of pressure cell with spectrophotometer or interferometer*

Owing to the small optical aperture in the DAC (ca. 0.25 mm^2 in area or larger) and in the piston-cylinder cell (Drickamer cell I, 0.028 in. and cell II,

TABLE 5

Anvil-type pressure cells (solids) used for optical spectroscopy ^a

Pressure limits (kbar) ^b	Optical Instrument	Windows	Wavelength range (μm)	Remarks	Ref.
100	Perkin-Elmer models 421, 350, Beckman IR-4	Diamond ^{c,d}	2-35	6 \times beam condenser	48
200	Perkin-Elmer models 225, 350, FTS-14	Diamond	0.27-40	6 \times beam condenser	62, 63
100	Perkin-Elmer model 301	Diamond	16-200	6 \times beam condenser	64
100	Beckman IR-11	Diamond	16-200	6 \times beam condenser	65
100	Beckman IR-12	Diamond ^d	2.5-16	6 \times beam condenser	65
100	Cary-14	Diamond	0.25-2.5	With or without a beam condenser	66
100	Digilab FTS 20 A	Diamond	1-1000	With beam condenser	68
100	Beckman FS-520 interferometer	Diamond	FIR \rightarrow 250	Light pipe necessary	67
100	Beckman #4260	Diamond ^d	2-50	With beam condenser	69
35	Michelson Interferometer	Quartz		Cube-anvil type cell	70
50 ^f	(?)	Diamond	NIR	Cube-anvil type cell; sample contained in NaCl; uses quartz or sapphire for lower pressures	71
150	FTS-14	Diamond	2.5-200	298-673 K	e(1)
200	PE 421, 210, Cary 14R, Spex 1700	Diamond	0.2-40	To 973 K	e(2)
	FTS-14	Diamond	2.5-500		e(3)
10	Cary 14R	Diamond	0.19-5	123-623 K	e(4)
100	Perkin-Elmer model 225	Diamond		Refracting beam condenser	73

^a DAC can be used for liquid or solutions if a gasket is used between the anvils. ^b DAC can be used routinely to 100 kbar if diamonds are properly aligned. ^c Diamond-Type I has absorptions at 3 μm (weak), 4-5.5 μm (intense), 7-10 μm (intense); Type II has absorptions at 3 μm (weak), 4-5.5 μm (intense). ^d Sapphire windows may be used from 2-5 μm . ^e Personal communication: (1) R.J. Jakobsen, Battelle Memorial Inst.; (2) G.J. Piermarini, Nat. Bur. Stand.; (3) G. Carlson, Westinghouse, Pittsburgh, Pa.; (4) C.A. Angell, Purdue Univ. ^f Claimed to be used to 1273 K.

0.037 in.) a means of condensing the source beam becomes necessary. In the case of a grating double beam spectrophotometer a beam condensation process is used (usually from 4–6 \times condensation) [48,62–66]. In the case of interferometric measurements a light-pipe has been used both for the entrance energy and the exit energy in the far IR region [67]. Recently, a new Harrick 6 \times beam condenser has been interfaced with the Digilab 20A interferometer [68]. A 4 \times beam condenser has also been coupled with a Beckman Model no. 4260 [69].

Using diamonds as the optical windows puts a stringent requirement on the properties of the beam condenser. The critical angle of diamonds is 26°. As a result the beam condenser should condense the light in a cone having an angle less than 52°. Also, since the faces of the diamonds are so small, the spot size of the condensed light should be as small as feasible, 1 mm² or less. One can then be sure that most of the condensed light is reaching the sample between the two diamonds and is not clipped by the large size of the DAC. Adams and Sharma [73] have recently reported a refracting beam condenser for IR use with the DAC. The optical problems associated with IR spectroscopy with a DAC are discussed [73].

For Raman scattering experiments both the DAC and the piston-cylinder may be used without any condensation of source energy, since lasers are used as the exciting sources with narrow beam radii. The laser light can be focussed directly into the small optical aperture of the pressure cell without too much difficulty.

(iii) Instrumentation for Raman spectroscopy at high pressure

Both the piston-cylinder and anvil-type cells have been used for obtaining Raman spectra at high pressure. Although energy problems are severe in IR spectroscopy because of the small optical aperture in the high pressure cells, the advent of laser sources for Raman spectroscopy has overcome a great deal of these problems.

The first Raman spectra obtained in a DAC were made in 1968 [59,60]. The red \rightarrow yellow transition in HgI₂ followed. In both cases 0° scattering geometry was used, although it was cited that 180° scattering could be used [59]. The DAC was also used for the study of liquid Br₂ and CS₂ [61]. However, except for solids with high Raman scattering efficiencies, the final results were disappointing. Recently, the DAC has been used with certain modifications and with improved results [53]. Adams et al. used a tungsten carbide window in place of one of the diamonds in the DAC [53]. The details are illustrated in Fig. 6. Both 90° and 180° scattering geometries were used. One limitation is that the tungsten carbide limits the maximal pressures to ca. 30 kbar. The tungsten carbide allows the Raman intensity to build up by allowing the excitation energy to traverse twice through the sample and additionally acts as a mirror. It has been suggested that back-silvering of one diamond anvil would give comparable results in the DAC and allow the DAC to be used

Tables 15–19 list some ionic lattice frequencies [167]. Most of the frequencies for the transverse optical lattice modes (ν_{TO}) in ionic salts are found below 300 cm^{-1} . The capability of measuring vibrational spectra in the far-IR region under pressure allowed study of these vibrations for the first time in this manner. The longitudinal mode (ν_{LO}) is more difficult to study in the IR. It is not normally observed at 90° incident radiation. Berreman [168] observed the longitudinal mode for a thin film of LiF with an oblique incident radiation, and longitudinal optical modes of the silver halides have been studied by a similar technique [171]. The longitudinal modes can be observed with a diamond cell and highly converging oblique radiation arriving from the beam condenser. They appear as shoulders on the main, intense transverse vibrational bands, and are not easily studied with pressure in the IR, for they are less pressure sensitive than the transverse modes and, because of the high-frequency shift of the ν_{TO} band, become lost in the ν_{TO} envelope. In more covalent solids ν_{TO} approaches ν_{LO} , and in a homopolar covalent crystal, ν_{TO} may equal ν_{LO} . In this instance, a very broad absorption is observed, which shows very little frequency shift with pressure.

Figure 10 shows a comparison of several ν_{TO} frequencies with pressure. The ν_{LO} pressure dependence for NaF is shown in Fig. 11. In this system the separation between ν_{LO} and ν_{TO} is sufficiently large to make possible a determination of the pressure dependence of both optical modes.

In general, ionic lattice vibrations shift toward higher frequencies with increasing pressure, although red shifts can be observed. The shifts at pressures of up to 50 kbar may be considerable; however, not all ionic lattice vibrations show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure for simple cubic ionic solids, where the three crystallographic axes are equal, is given in eqn.

$$(1) \quad \gamma\chi\nu = (\partial\nu/\partial p)_T \quad (1)$$

where γ is the Grüneisen parameter, χ is the isothermal compressibility of the

TABLE 15
Lattice vibrations for alkali halides^a

Halide	$\nu_{\text{TO}} \text{ (cm}^{-1}\text{)}$	Halide	$\nu_{\text{TO}} \text{ (cm}^{-1}\text{)}$	Halide	$\nu_{\text{TO}} \text{ (cm}^{-1}\text{)}$
LiF	307	NaI	117	RbCl	118
LiCl	191	KF	190	RbBr	88
LiBr	159	KCl	141	RbI	77
NaF	246	KBr	113	CsCl ^b	99
NaCl	164	KI	98	CsBr ^b	74
NaBr	134	RbF	156	CsI ^b	62

^a Ref. 169. ^b Ref. 170.

TABLE 16

Lattice vibrations for several other ionic crystals^a

	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})
TlCl	63	158
TlBr	43	101
AgCl	106	196
AgBr	79	138
MgO	401	718
NiO	401	580
CoO	349	546
MnO	262	552

^a IR data from S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.

TABLE 17

Lattice vibrations for II-VI compounds^a

	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})
ZnO	() 377 (⊥) 406	575 589
ZnS	278	350
ZnSe	205	253
ZnTe	179	206
CdS	239	306
CdSe	170	211
CdTe	125	151

^a IR data from S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.

TABLE 18

Lattice vibrations for III-V compounds^a

	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})
InSb	185	197
InAs	219	243
InP	304	345
GaSb	231	240
GaAs	269	292
GaP	367	403
AlSb	319	340
AlP	440	501
AlN	667	916
BP	820	834
BN	1056	1304

^a From S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.

TABLE 19

Lattice vibrations for IV—IV compounds^a

	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})
Diamond	1332 ^b	1332 ^b
Silicon	520 ^b	520 ^b
Germanium	301 ^b	301 ^b
SiC	793 ^c	970 ^c

^a From S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.^b Raman frequencies. ^c IR frequencies.

solid, and ν is the frequency of the lattice mode. For non-compressible solids, it is possible that only small shifts will occur. For example, the lattice modes of zirconium and hafnium oxides failed to show significant shifts at 40 kbar [67]. It is also possible that the pressure effects may be different in noncubic crystals having different axes parameters, depending on which axis becomes compressible [172,173].

The data obtained from studies of the pressure dependence of the $\kappa \simeq 0$

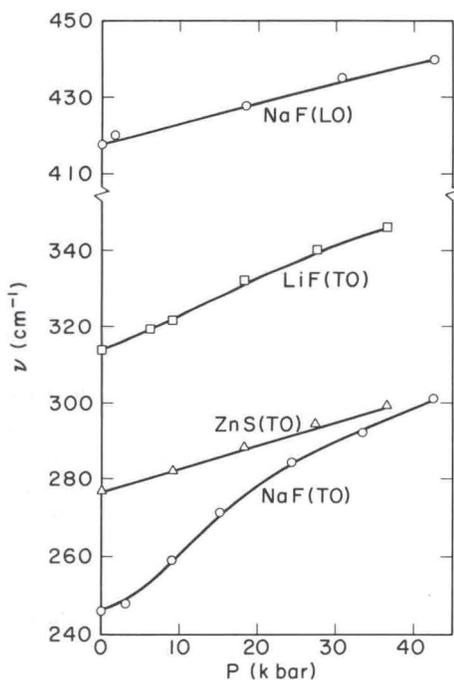


Fig. 10. Pressure dependencies of several lattice vibrations [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

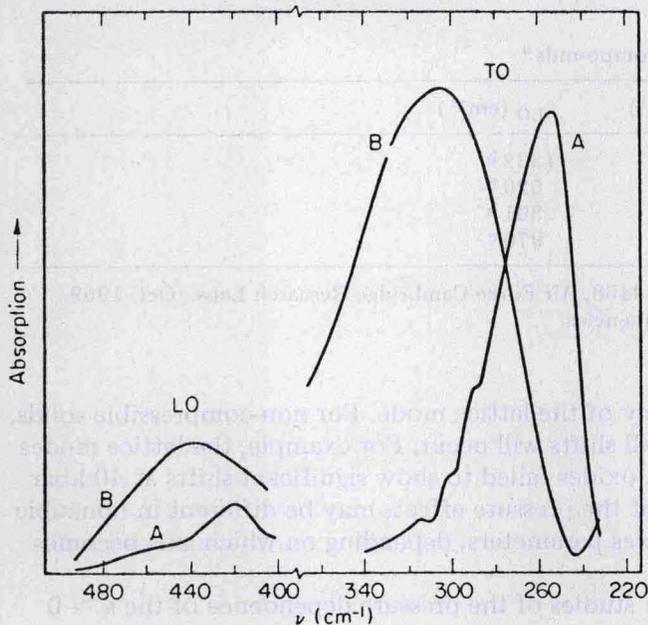


Fig. 11. Comparison of TO and LO modes in NaF with and without pressure [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

lattice vibrations of ionic crystals [174], when combined with data from studies of these modes with temperature [175], may allow calculation of the anharmonic interactions taking place, and contribute to a better understanding of the lattice dynamics of these solids. It is possible to distinguish between the purely volume-dependent contribution and the contribution from various anharmonic terms in the crystal Hamiltonian [176]. Fig. 12 shows a plot of $\ln \nu/\nu_0$ vs. $\ln V/V_0$ for several optical modes. The data have been obtained from pressure and high-temperature studies [174–176], P - V data from Pagannone and Drickamer [177], and from Cline and Stephens [178]. It can be observed that the straight line extrapolated from the pressure domain does not coincide with the line obtained from the temperature data. The difference may be attributed to the anharmonic contribution to the frequency shift (known as the self-energy shift), which increases steadily with increasing temperature of LiF. A similar analysis was made for KBr and in this crystal the self-energy shift is negligible. Results obtained for RbI using other techniques [175,179] also indicated negligible self-energy shifts.

The results obtained for the Grüneisen parameters for the long-wavelength optical modes from eqns. (1) and (2)

$$\lambda_{j(k)} = -\partial \ln \nu_j(k) / \partial \ln V \quad (2)$$

are given in Table 20. The agreement with the calculations made from those

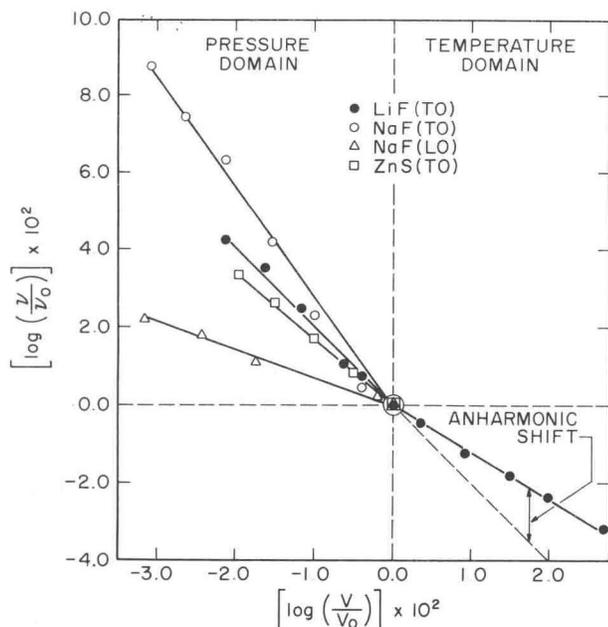


Fig. 12. Plot of $\ln \nu/\nu_0$ vs. $\ln V/V_0$ for several optic modes [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

assuming a rigid-ion model with central forces incorporating repulsion terms of the Born-Mayer [$\exp(-r/p)$] and inverse-power (r^{-n}) type is good. The results using Cowley's theory give somewhat larger values of γ .

The pressure dependencies of two phases of a solid can be determined by these techniques. Such studies have been made with KBr and KCl [176]. Figure 13 shows the TO mode of KCl as a function of pressure and illustrates the difficulty of studying phase transitions. The pressure gradient across the

TABLE 20

Grüneisen parameters for the long-wavelength optical modes

	Experimental		Calculated				
	Eqn. (1)	Eqn. (2)	Born-Mayer ^a	r^{-n} repulsion ^b	Cowley ^c	Model I ^d	Model II ^d
LiF	2.15	2.59	2.44	3.46			
NaF	2.80	2.95	2.43	3.00			
KBr		2.83	2.52	2.95	3.27	~3.0	~2.6
KCl		2.46	2.52	2.92			

^a Ref. 180. ^b Ref. 181. ^c Ref. 182. ^d Ref. 183.

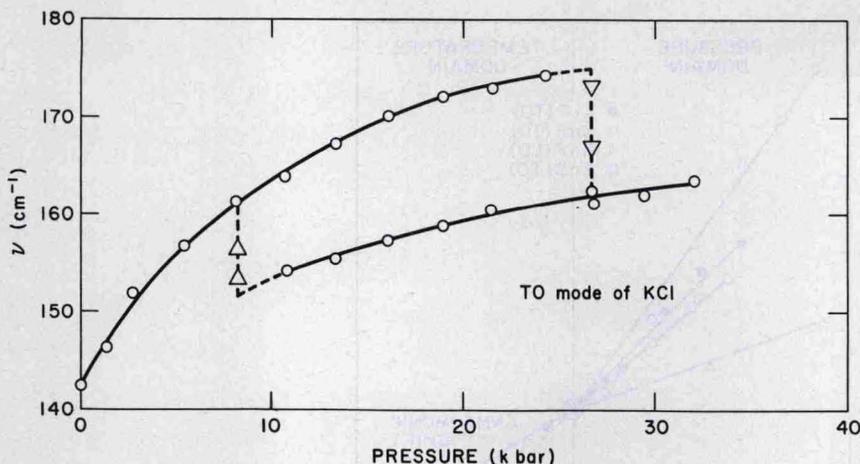


Fig. 13. TO mode of KCl as a function of pressure [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

diamond anvils prevents the detection of a sharp transition pressure and both phases appear over a range of pressures. The high-pressure phase (CsCl structure) appears at 16 kbar for KBr and at 24 kbar for KCl. The conversion to the the high-pressure phase is complete at 26 and 30 kbar for KBr and KCl, respectively. For a limited average pressure range the TO mode of both the low- and high-pressure phases can be detected, with a gradual decrease in the intensity of the low-pressure phase and an increase in that of the high-pressure phase. With the reduction of pressure, the frequencies of the CsCl phase do not coincide with those determined from increasing pressures (maximum experimental error $\pm 2 \text{ cm}^{-1}$). The low-pressure phase does not reappear until 11 and 16 kbar for KBr and KCl, respectively. Some of these discrepancies can be attributed to the sluggishness of the system and friction created within the cell.

The vibrational frequency decreases at the transition pressure by about 10–12%. The ratio of TO frequency of the CsCl phase to that of the TO frequency in the NaCl phase should equal the square root of the coordination number of each phase; e.g., $\frac{3}{8}^{1/2}$ or 0.87. The observed ratio for KBr is 0.88 and that of KCl is 0.92.

It has been found [184] that the $k \approx 0$ TO frequency of the alkali halides of NaCl structure is proportional to $(a/\chi\mu)^{1/2}$, where a is the lattice constant, μ is the reduced mass per unit cell, and χ is the compressibility. The same is true for the CsCl structure, as illustrated in Fig. 14.

Pressure studies of mixed crystals have recently been reported for $\text{CdS}_{1-x}\text{Se}_x$, $\text{ZnS}_{1-x}\text{Se}_x$ [185] and $\text{KCl}_{1-x}\text{Br}_x$ [186]. In both the two-mode system $\text{ZnS}_{1-x}\text{Se}_x$, and the one-mode system $\text{KCl}_{1-x}\text{Br}_x$, the pressure dependencies of the various mixtures of the mixed crystals parallel those obtained for the pure components. Figure 15 illustrates the pressure dependence

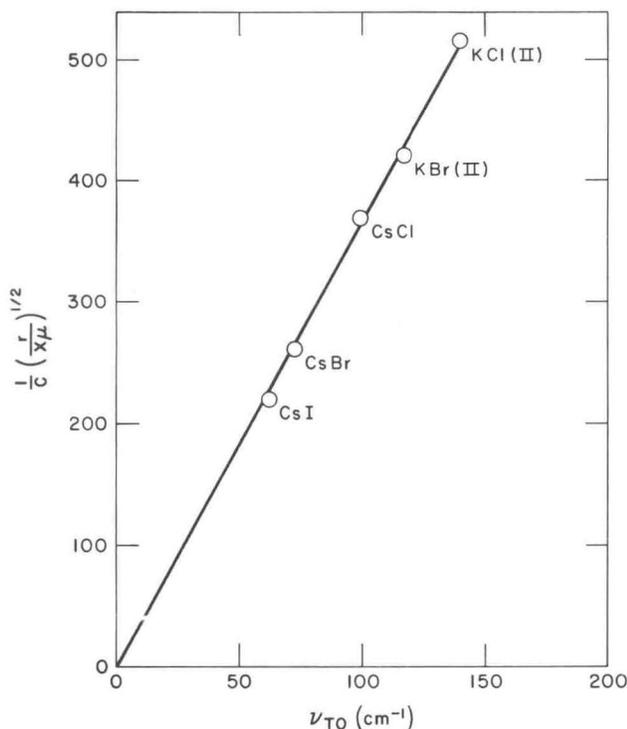


Fig. 14. Plot of TO mode frequency for several CsCl-type salts vs. $1/c(r/x\mu)^{1/2}$ [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

of the high frequency mode in the $ZnS_{1-x}Se_x$ system.

Certain molecular lattice modes were investigated by McDevitt et al. [67] and Fondere et al. [187]. The experiments are more difficult to perform since a thicker sample is needed, and gaskets are necessary to accomplish this. Molecular lattice vibrations have been observed to also shift toward higher frequencies with increasing pressure. Raman experiments [188] have demonstrated that molecular lattice vibrations are more sensitive to pressure than ionic lattice modes, as expected.

Pressure dependencies of KI, RbI and their mixed crystals have been determined [189]. The mode Grüneisen parameters were determined and compared well with the calculated parameters from a rigid ion model using the Born-Mayer type potentials. Similar measurements have also been made for IR-active phonon modes in alkali-earth fluorides [190]. The pressure dependence of the Raman spectra of the alkaline-earth fluorides is also available [191]. Several anti-fluorite structures have been studied at high pressures (e.g., Mg_2Si , Mg_2Ge , Mg_2Sr) [192].

First and second order Raman spectra have recently been obtained on hexa-

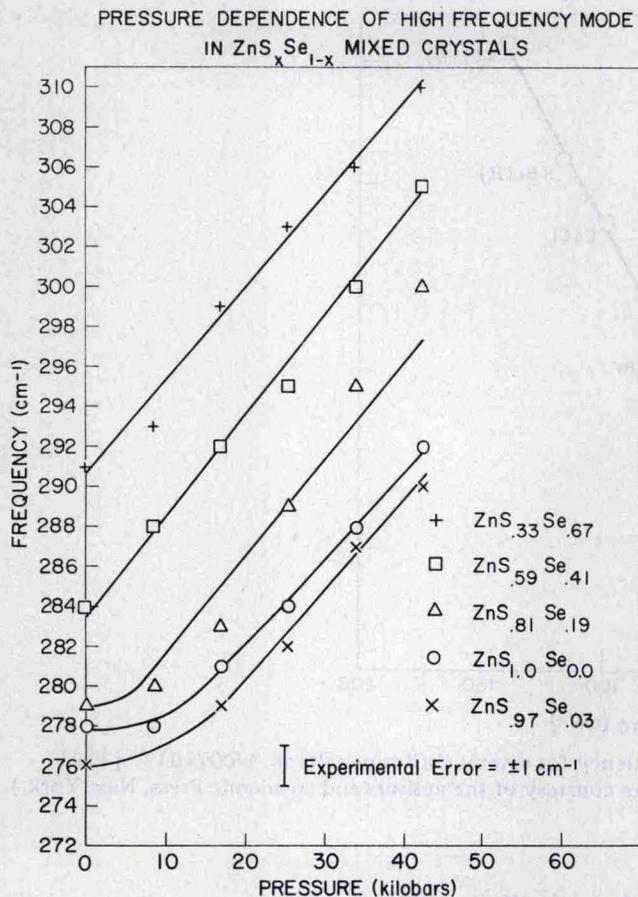


Fig. 15. Pressure dependencies of high frequency mode in $ZnS_{1-x}Se_x$ mixed crystals [185]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

gonal ZnS (wurtzite) at pressures to 40 kbar [193]. No phase transformation to a cubic phase was observed. The Grüneisen parameters were found to be 0.99 for the ν_{LO} mode and 1.81 for the ν_{TO} mode. For the ν_{TA} mode the value ranged from -1.79 to 2.38 in the second-order spectrum. The splitting between ν_{TO} and ν_{LO} decreases with pressure. Raman (one- and two-phonon) spectra of GaP at pressures to 135 kbar were determined [194]. Mode Grüneisen parameters were calculated. Raman and far-IR studies to 45 kbar of the phase transition in paratellurite (TeO_2) were made recently [195]. At the phase transition at 9 kbar an E mode at 122 cm^{-1} splits into two components in the IR and Raman spectra. These results aided in assigning the various phonon modes in TeO_2 . Raman spectra to 4 kbar were obtained for TiO_2

(rutile) [86]. Grüneisen parameters for each lattice mode were obtained. The B_{1g} phonon mode was found to have a negative pressure dependency. These results agree with earlier pressure measurements made to 40 kbar, which demonstrated a $d\nu/dp$ for this mode as $-0.3 \pm 0.1 \text{ cm}^{-1} \text{ kbar}^{-1}$ [196]. This mode softens as well with decreasing temperature, although only slightly. The unusual pressure dependency for this vibration may have important implications relative to pressure-induced phase transitions in rutile, as well as in other crystals with this structure.

(iii) Coordination compounds

Interest in solid coordination compounds has centered on the behavior of various vibrational transitions under high pressures. Considerable interest has also developed in changes occurring with pressure in spin states and in oxidation states, and to identify these changes with far IR spectroscopy. Perhaps of most significance are the structural transformations which pressure has induced. The latter effects have served to test the theoretical predictions of Pearson [197] and Bader [198] regarding stability of various geometrical configurations. It is also possible that these studies provide a foundation for anticipated ultra-high pressure measurements of minerals.

(1) High pressure effects on vibrational transitions

As more research involving high pressure effects accumulates with time, it has become clear that certain vibrations are more sensitive to pressure than others. For example, vibrations which involve expansion of molecular volume appear to be more sensitive to pressure. Attempts to quantify the behavior of vibrations with pressure may never be realized for the application of pressure to solids involves many factors, and screening these factors may be an impossible task. Such factors as packing effects, compressibilities, nature of bonds (ionic vs. covalent), crystal field stabilization energy, steric effects, electronic repulsions, electronic delocalization, and other effects all contribute toward pressure-sensitivity of various vibrations in a molecule.

Examples of pressure effects on vibrations in different molecules will be discussed in the following sections.

(a) Ligand vibration. Relatively little attention has been paid to the effects of pressure on ligand vibrational modes. In a study of pyrazine and its complexes up to 72 kbar several observations could be made [199]. (1) Ligand bonds showed blue shifts and were less sensitive than the bands of the complexes. (2) Some bands showed splitting. (3) Although the vibrations in the ligands and their metal complexes were not the same, the pyrazine spectrum under pressure showed similarities to spectra of the corresponding metal complexes. This may appear to indicate that metallic complexation involves a pressure effect. The splitting of bands can be accounted for in terms of a lower symmetry or involving factor-group splitting. A new study of dihalocy-

clohexanes in the far IR region has recently appeared [200]. Pressure dependencies of the Raman and IR spectra of α -, β -, γ - and δ -octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine have been made [201].

(b) *Metal sandwich compounds.* In a study on the effects of pressure (to 35 kbar) on the IR active skeletal vibrations of metal sandwich compounds, it was found that the $\nu(\text{M-ring})_{\text{asym}}$ vibrations are more sensitive to pressure than the ring tilt mode [202]. Table 21 shows the pressure dependencies in these compounds.

(c) *Metal-halogen stretching modes.* In complexes displaying both asymmetric and symmetrical metal-halogen stretching vibrations it was demonstrated that pressure effects (to 50 kbar) on the symmetrical vibration are more effective [203]. Although only minor shifts are observed, the symmetrical mode shows large decreases in intensity. The compounds studied included the following: 1. norbornadienedichloroplatinum(II), $(\text{C}_7\text{H}_8)\text{PtCl}_2$; 2. 2,2',2''-terpyridinedichlorozinc(II), $(\text{terpy})\text{ZnCl}_2$; 3. bis(α -picoline)dichlorocobalt(II), $(\text{C}_6\text{H}_7\text{N})_2\text{CoCl}_2$; 4. tetraphenylarsenic trichlorostannate(II) $[(\text{C}_6\text{H}_5)_4\text{As}][\text{SnCl}_3]$; 5. tetraphenylarsenic trichlorogermanate(II), $[(\text{C}_6\text{H}_5)_4\text{As}][\text{GeCl}_3]$; 6. norbornadienedibromoplatinum(II), $(\text{C}_7\text{H}_8)\text{PtBr}_2$; 7. 2,2',2''-terpyridine-bromozinc(II), $(\text{terpy})\text{ZnBr}_2$; 8. bis(pyridine)dibromocobalt(II), $(\text{C}_5\text{H}_5)_2\text{CoBr}_2$; 9. bis(α -picoline)dibromocobalt(II), $(\text{C}_6\text{H}_7\text{N})_2\text{CoBr}_2$.

Results with the bromides indicate that the metal-bromine stretching mode behaves similarly to the metal-chlorine mode under pressure. However, since the assignments for the ν_{MBr} vibration are less well known because of the close proximity of the metal-nitrogen stretching vibration, further studies are necessary. Figure 16 shows the low frequency $\nu\text{M-X}_{\text{asym}}$ and $\nu\text{M-X}_{\text{sym}}$ vibrations $[\phi_4\text{As}][\text{SnCl}_3]$ as a function of pressure.

Lever has reported in a series of papers [204a] that metal-ligand vibrations in coordination complexes upon cooling to 80 K, increase in frequency relative to the "pure" ligand vibrations. The cooling effects are very similar to those observed with the application of high pressure (Sections (1)(a) and (1)(c))

TABLE 21

Pressure effects on skeleton modes of metal sandwich compounds [202]

	Ring tilt (cm^{-1})		$\nu(\text{M-ring})$ (cm^{-1})	
	Ambient pressure	35 kbar	Ambient pressure	35 kbar
$\text{Fe}(\text{Cp})_2$	491	494	461	474
$\text{Ru}(\text{Cp})_2$	447	476	381	390
$\text{Mn}(\text{Cp})_2$	432	437	409	420
$\text{Cr}(\text{C}_6\text{H}_6)_2$	487	491	453	475

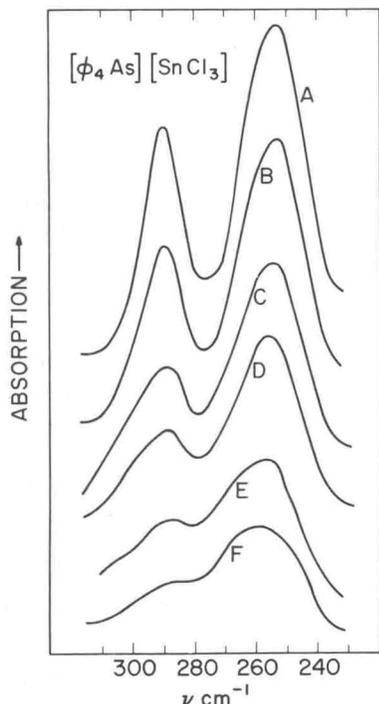


Fig. 16. Frequency of $\nu_{\text{SnCl}_3\text{asym}}$ and $\nu_{\text{SnCl}_3\text{sym}}$ in $[\phi_4\text{As}][\text{SnCl}_3]$ as a function of pressure [203]. (Figure reproduced through the courtesy of the authors and the American Chemical Society, Washington, D.C.)

above). The use of low temperature has been suggested as a guide to band assignments in these complexes.

(d) *Metal-halide bridging vibrations.* Complexes of the type CoL_2X_2 , where $\text{L} = \text{py}$, 4-Cl(py) or 4-Br(py) and $\text{X} = \text{Cl}$ or Br are known to exist in polymeric and monomeric forms. The monomeric forms are tetrahedral and blue or green colored, and the polymeric forms are octahedral and lilac colored. The assignments for bridged cobalt-halide stretching vibration ($\nu_b\text{CoX}$) and terminal vibration ($\nu_t(\text{CoX})$) in these complexes were made possible by pressure studies to 28 kbar [204]. The $\nu_b\text{CoX}$ vibrations manifested appreciable blue shifts as opposed to the $\nu_t\text{CoX}$ vibration. The $\nu(\text{Co-N})$ shifts appear to be smaller, of the order of 18 cm^{-1} .

(e) *Complex compounds.* High pressure studies of some hexa-ammine complexes of Ni(II) and Co(II) have been made [205]. The pressure studies to 40 kbar for the Ni(II) complexes were different than low-temperature studies, and indicated a phase change and a lowering of symmetry being involved.

Complex halides like K_2PtCl_4 , K_2PdCl_4 , K_2PtCl_6 and K_2PdCl_6 have been studied at high pressure (ca. 33 kbar) [206]. In the K_2MCl_4 complexes of D_{4h}^1 symmetry [207] it was found that the E_u internal vibrations were more pressure sensitive than the A_{2u} internal vibration in the MCl_4^{2-} ions. The most pressure sensitive external mode was the translational lattice mode along the long axis a_0 , while the mode along the short axis c_0 was less pressure dependent. It was concluded that with an increase in pressure, contraction occurred along the a_0 axis, while a contraction or even expansion occurred along the c_0 axis. The X-ray work of Drickamer may lend some substantiation to these conclusions, as in the tetragonal solids MnO_2 and SnO_2 pressure contracts along the a_0 axis while the c_0 axis expands [172,173].

In the cubic crystals (O_h^5) K_2MCl_6 , where $M = Pt(II)$ or $Pd(II)$, differentiation between internal and external modes was less certain, although the lattice mode appeared to be slightly more pressure sensitive. A series of transition-metal hexahalides was also studied under pressure to 20 kbar, and Adams and Payne [208] concluded that the pressure sensitivity followed the order $\nu_2 > \nu_4 > \nu_3$. For M_2PtCl_6 , where $M = K, Rb, Cs, Tl$ or NH_4 , the pressure sensitivity of the $\nu(Pt-Cl)$ modes of vibrations decreased in the order $A_{1g} > E_g > F_{1u}$ at pressures to 20 kbar [209].

Several complex cyanides have been investigated at high pressures up to 30 kbar, and the effects studied by IR spectroscopy [210]. The compounds examined were $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, $K_2[Hg(CN)_4]$, $Zn(CN)_2$, $Cd(CN)_2$ and $Hg(CN)_2$. Pressure effects were studied by examining the CN stretching region as well as the metal-CN stretching region ($200-600\text{ cm}^{-1}$). For the $M(CN)_4^{2-}$ tetrahedra it was found that the degeneracy of the F_2 vibrations was removed with pressure. It was concluded that for $M = Zn$ or Cd the symmetry had lowered to D_{2d} , while for $M = Hg$ to D_2 or C_{3v} . Lower symmetry resulted for $Zn(CN)_2$. However, an increase in symmetry took place for $Hg(CN)_2$ and $Cd(CN)_2$.

A far IR study of salts of SeX_6^{2-} , where $X = Cl$ or Br and TeX_6^{2-} where $X = Cl, Br$ or I at pressures up to 40 kbar was made [211]. All bands were observed to show blue shifts with the ν_4 bending mode exhibiting the most dramatic effect. For some compounds which did not show ν_4 , the band appeared with increased pressure. In most cases which showed ν_4 at ambient pressures, the vibration eventually disappeared with increased pressure. The results were explained on the basis of an anion-cation bonding scheme, which allows a pressure-dependent delocalization of the inert-pair electrons throughout the lattice.

(f) *Miscellaneous.* In a Raman study of metal carbonyls the A_{1g} $\nu(CO)$ shifted 12 cm^{-1} at 25 kbar in tungsten carbonyls, while the E_{1g} mode was substantially less sensitive [212].

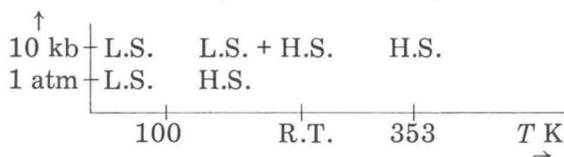
(2) Pressure effects on spin states

A number of changes of oxidation state and spin states caused by pressure

have been reported by Drickamer and Frank [27]. In these cases Mössbauer or absorption spectroscopy was used as the diagnostic tool to observe the changes. For changes in solutions, see Sinn [26].

Recently, several systems have been examined using vibrational spectroscopy as the diagnostic tool to identify spin-state equilibria in the solid state. In these examples the far IR region, and in particular, the metal–ligand vibration was followed with pressure to determine a change from a high-spin to a low-spin state. The high-spin, metal–ligand vibration occurs at lower energy than the low-spin, metal–ligand vibration. In some instances low temperatures are used with pressure to facilitate the conversion.

The complex $\text{NiBr}_2(\text{Bz}\phi_2\text{P})_2$ was converted at 12 kbar from a high-spin, distorted tetrahedral molecule to a low-spin, square-planar configuration [213]. In this complex a structural change as well as a spin-state conversion occurred. $\text{Co}(\text{nnp})(\text{NCS})_2$, where $\text{nnp} = \text{Et}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2\text{P}\phi_2$, was converted at 10 kbar and 150 K from the high-spin to low-spin state [214]. The relationship of the equilibria with temperature and pressure is shown below.



The $\text{Fe}(\text{phen})_2\text{X}_2$ and $\text{Fe}(\text{bipy})_2\text{X}_2$ complexes, where phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine and $\text{X} = \text{Cl}^-$, Br^- , N_3^- , NCO^- , OAc^- , HCOO^- exist in high-spin states [215]. The complexes $\text{Fe}(\text{phen})_2(\text{NCS})_2$, $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ and $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ were studied at high pressures and/or low temperature [215]. Complete conversion with pressure to low spin did not occur. However, the mixtures of high-spin and low-spin forms maintained at high pressures, could be converted to the low-spin state if the sample was cooled to 100 K. The high-spin state can be converted to the low-spin state directly with cooling to 100 K. The results parallel those obtained by Fisher and Drickamer [216] using Mössbauer techniques for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{phen})_2(\text{NCSe})_2$. High-spin–low-spin crossovers with pressure have also been observed for tri(N-ethyl-N-phenyldithiocarbamato)iron(III) [217,218], and represent the first pressure conversions of Fe(III) to low-spin. These results may have some consequences in problems relating to the earth's mantle.

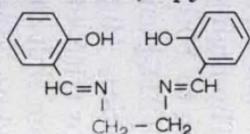
The results of the low temperature conversion to low spin may be explained in terms of a strengthening of the Fe–N (phen or bipy) and Fe–N (NCS and NCSe) bonds due to back-donation of the t_{2g} electrons of the metal to the π^* orbitals of the organic ligand and NCSe. This mechanism may also be present at the outset of pressure applications, but the back-donation of the metal is reduced with increasing pressure by the accessibility of the π electrons from the ligand to the ligand π^* orbitals [27]. Table 22 summarizes high-pressure spin-state conversions.

Spin interconversions [215–218]

Central atom	C.N.	High spin (No. of unpaired e's)	Conversion	pressure (kbar)	Exp
	5	3	High Spin → Low Spin	21	NO
	6	2	High Spin → Low Spin	18	Ske
	6	2	High Spin → Low Spin	8–10	Ske
	6	2	High Spin → Low Spin	15	Ske
	5	3	High Spin → Low Spin	4	Ske
	4	2	High Spin → Low Spin ^a	12	Ske
	6	5	High Spin → Low Spin	35	Ske

on also occurs.

= phenanthroline; bipy = bipyridyl; nnp = $\text{Et}_2\text{N}-(\text{CH}_2)_2-\overset{\text{H}}{\text{N}}-(\text{CH}_2)_2\text{P}\phi_2$; Bz = benzyl; EPDTC = N-ethyl-N-phenyldithiocarbamate.



(3) Ligand isomerism

Ligand isomerism is well characterized. Most of the studies have involved equilibria between the two forms in solution. Little is known of these equilibria in the solid state. In solid $\text{Ni(en)}_2(\text{NO}_2)_2$ at a pressure of 30 kbar, the violet form (obtained at ca. 120°C) was transformed to the red form [219]. The red isomer is the dinitro form, while the violet isomer is the dinitrito form. The 560 nm band was used to monitor the transformation.

(4) Pressure reduction

In a study at high pressure of $[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{NCS})_6]$ (ref. 220) it was observed that a pressure-dependent reduction of Fe(III) to Fe(II) occurred, confirming the Mössbauer studies of Fung and Drickamer [221]. The reduction was characterized by the appearance of a new band at 238 cm^{-1} at lower frequency than the $295, 270\text{ cm}^{-1}$ vibrations attributed to the $\nu_{\text{Fe}} + 3_{-\text{N}}$ mode. A similar reduction [222] was found with pressure for $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ from a study of the ν_{CN} vibration in the $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ species. No evidence was obtained, which could be attributed to any ligand isomerization occurring.

Other oxidation—reduction effects of pressure using Mössbauer techniques have been noted by Drickamer and Frank [27].

(5) Structural conversions with pressure

Most structural interconversions have been studied in solution. NMR spectroscopy has been an ideal tool for such studies because often the equilibrium established between labile structures can be shifted in favor of one structure by a change in temperature. Until recently, few high-pressure studies of solid-state structural interconversions of complexes have used vibrational and electronic spectroscopy. The Mössbauer effect has, however, been used extensively by Drickamer and Frank [27].

It is reasonable to assume that solid-state interconversions involve considerably larger energy effects than those observed in solution. For solid complexes, in addition to the symmetry effects discussed above, molecular packing, lattice forces, ligand flexibilities, metal—ligand bond distances, $d-d$ electronic transition energies, orbital overlap and orientation effects, and hydrogen bonding among other factors must also be considered. High pressure is known to affect many of these factors [27,223,224] and will favor the structure with a smaller packing volume. High-pressure effects are observed to shorten the metal—ligand bond distance and to increase the average ligand field strength [223–225]. In the cases involving high-spin complexes, this increase in ligand field energy may be sufficient to overcome the electron spin pairing energy and produce a low-spin complex.

Of particular interest is the effect of high pressure on the IR absorption bands of a solid complex. A reduction in the metal—ligand bond distance shifts the vibrational bands to higher energy. For bending modes, which might possibly transform one structure into another, the effects of pressure

may be smaller and conceivably the associated band may shift to a lower energy. It is also possible that, at high pressure, normally forbidden modes may become allowed (in a lower site symmetry), and if this mode yields a structural interconversion, the vibration may then become allowed. Thus, it is of interest to examine the solid-state rigidity of various molecules with differing stereochemical configurations at high pressure.

(iv) High-pressure studies of several solids in different symmetries

Solid-state structural transformations obtained for several representative solids at high pressure are presented in Table 23. From these results, it may be concluded that structural interconversions are possible for transition-metal complexes in the solid state. The interconversions are all reversible, with the exception of that for the $\text{Ni}(\text{Qnqn})\text{Cl}_2$ complex.

We have proposed a new scheme for the classification of the types of behavior observed in transition-metal compounds at high pressure (see Table 24) [226]. The four behavior classes are based primarily upon the presence or absence of a structural and/or electronic change in the complex between ambient and high pressure. Class 1 compounds exhibit neither large structural nor electronic changes, but they would include compounds which show small effects, such as slight unit cell contractions, minor crystallographic changes in space group, small changes in crystal-field parameters, and small shifts in charge-transfer bands. Class 2 compounds exhibit significant structural changes with, at most, minor electronic changes, whereas the reverse situation holds for class 3 compounds. Classes 2 and 3 may be further subdivided as shown in Table 24 depending upon the absence or presence of a coordination number change, etc. Class 4 includes compounds with both electronic structural changes at high pressure and, of course, could have many subdivisions if necessary based upon the presence or absence of each electronic and structural factor.

The behavior of various selected transition-metal complexes at high pressure will now be discussed in terms of their coordination number and behavior type.

(1) Four-coordinate complexes

The two complexes, dichloro- and dibromobis(benzylidiphenylphosphine)-nickel(II), $\text{Ni}(\text{BzPh}_2\text{P})_2\text{X}_2$, may each be prepared as both red and green isomers [237]. Both of the red complexes are the diamagnetic square-planar forms of the complex. However, there are substantial differences between the two green isomers. The green bromide isomer (with a reduced magnetic moment of $2.70 \mu\text{B}$ at room temperature) has been shown by single-crystal X-ray analysis [238] to contain one square planar and two tetrahedral nickel atoms per unit cell. The magnetic moment of the green chloride isomer ($3.23 \mu\text{B}$ at room temperature) and its spectroscopic properties reveal that it is fully tetrahedral in coordination geometry.

TABLE 23

Solid state structural transformations induced by high pressure [226]

Compound	C.N.	Symmetry ^a ambient pressure	Structural transformation with pressure	Transformation press. (kbar)	Spectroscopic probe	Remarks
Ni(Bz ϕ ₂ P) ₂ Cl ₂	4	Pure T _d	No change		Electronic FIR	
Ni(Bz ϕ ₂ P) ₂ Br ₂ ^b	4	1/3 Planar (Square) 2/3 T _d	Planar (square)	20	Electronic FIR	Reversible
Ni(Qnqn)Cl ₂	4	Distorted T _d	Binuclear, SQP [Ni(Qnqn)Cl ₂] ₂	2	Electronic FIR	Irreversible
CuCl ₄ ²⁻ ^c	4	Flattened T _d	Planar (square)	20	FIR	Reversible
Ni(CN) ₅ ³⁻ ^d	5	SQP + TBP	SQP	7	IR in 4 μ m	Reversible
[NiLX] ⁺ , NiLX ₂ , [NiL ₂ X] ⁺ NiL ₃ X ₂	5	SQP + TBP	TBP	Onset of press.	Electronic	Reversible

^a Local symmetry around central metal atom considered. ^b Ni(Bz ϕ ₂P)₂I₂ inferred to be similar Ni(Bz ϕ ₂P)₂Br₂ from magnetic moment.

^c Cation is (CH₃)₂CHNH₃⁺ or Cs⁺. ^d Cation is Cr(en)₃³⁺; compound is [Cr(en)₃Ni(CN)₅] 1.5 H₂O.

Abbreviations: Bz = benzyl; ϕ = phenyl; Qnqn = *trans*-2-(2'-quinoly1)methylene-3-quinuclidione; L = organic ligand; X = halogen or pseudo halogen; T_d = tetrahedral; SQP = square pyramidal; TBP = trigonal bipyramid.

TABLE 24

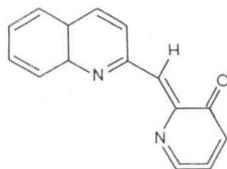
Behavior classes for pressure-induced solid-state changes [226]^a

Behavior class	Structural change		Electronic change		Examples	Ref.
	Geo-metric change	C.N. change	Spin-state change	Oxidation state change		
1	No	No	No	No	Green Ni(BzPh ₂ P) ₂ Cl ₂ [Ni(Qnqn)(Cl) ₂] ₂ Co(Qnqn)Cl ₂ FeS ₂	213 227 225 228
2A	Yes	No	No	No	Several CuCl ₄ ²⁻	229, 230
2B	Yes	Yes	No	No	Ni(CN) ₅ ³⁻ Ni(Qnqn)Cl ₂ , Co(py) ₂ Cl ₂	231 204, 227
2C	Yes	No	Yes	No	Green Ni(BzPh ₂ P) ₂ Br ₂	213
3A	No	No	Yes	No	Mn(Fe)S ₂ Fe(phen) ₂ (N ₃) ₂ Fe(phen) ₂ (NCS) ₂	232 216 215, 216, 233
3B	No	No	No	Yes	Fe(acac) ₃ Cu(OXin) ₂ Hemin	234 235 27
4	Yes			Yes	Co(NO)(Ph ₂ CH ₃ P) ₂ Cl ₂	236

^a A modified version of that in ref. 226 appears above.Abbreviations: C.N. = coordination number; Bz = benzyl; Qnqn = *trans*-2-(2'-quinolyl)methylene-3-quinuclidione; py = pyridine; ArgH = (H₂N)₂CNH(CH₂)₃CHNH₂COO⁻; aca = acetylacetonate; OXin = 8-hydroxyquinoline.

Both the electronic and IR absorption spectra of the two paramagnetic green isomers were studied as a function of pressure [213]. The green Ni(BzPh₂P)₂Cl₂ isomer retains its tetrahedral coordination geometry at all pressures and shows no indication of any conversion to a square-planar geometry at high pressure. However, the green Ni(BzPh₂P)₂Br₂ isomer is transformed from the above-mentioned mixture of tetrahedral and square-planar coordination geometries at ambient pressure, to the purely square-planar red isomer at high pressure [213]. This reversible pressure-induced structural transformation is essentially complete at ca. 20 kbar and represents class 2C behavior. In this instance, the change in the spin state of the nickel ion occurs as a result of the geometric structural change and not directly as a consequence of the high pressure.

In another high-pressure study [227], it was possible to irreversibly convert the paramagnetic violet pseudotetrahedral nickel complex, $\text{Ni}(\text{Qnqn})\text{Cl}_2$, into its yellow paramagnetic binuclear $[\text{Ni}(\text{Qnqn})\text{Cl}_2]_2$ isomer. In these complexes, the Qnqn ligand is *trans*-2-(2'-quinoly)methylene-3-quinuclidinone.



Qnqn

Both the yellow and violet isomers have been prepared directly [227], and the X-ray structure [239] of the yellow binuclear isomer has revealed two bridging and two terminal chlorine ligands and bidentate coordination for Qnqn. The application of pressure to the violet monomeric complex causes the two nickel-chloride nonbonded distances to decrease to a point where the two additional bridging chlorine bonds are formed, and the yellow binuclear complex results. The spectrum of the complex clearly reveals the irreversible changes in both the $\nu_{\text{Ni}-\text{Cl}}$ and $\nu_{\text{Ni}-\text{N}}$ vibrational bands as a function of pressure. The electronic absorption spectrum of the violet isomer also reveals the expected changes in the *d-d* bands at high pressure.

This is the first example of such an irreversible pressure-induced structural transformation known to us. The irreversibility of this transformation may result from the bond energy of the two additional chlorine bridging bonds, which would make the reverse transformation thermodynamically unfavorable. This transformation involves both a change in coordination number and a change in coordination geometry and represents class 2B behavior. The yellow dimeric $[\text{Ni}(\text{Qnqn})\text{Cl}_2]_2$ exhibits only minor changes at high pressure and is in class 1 [226,227].

The room-temperature preparation of $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$ has been found [240] from X-ray studies to contain one copper ion in a square-planar configuration and two copper ions arranged in tetrahedrally distorted configurations. The crystal is held together by hydrogen bonding from the isopropylammonium ions. At high pressures the coordination geometry of the two tetrahedrally distorted copper ions is reversibly converted to a square-planar geometry [229]. The conversion is observed as a change in the $\nu_{\text{Cu}-\text{Cl}}$ and δ_{ClCuCl} vibrational bands. Confirmation for the conversion was also found in the change occurring in the electronic region [229,230]. A similar structural conversion is also found [230] in Cs_2CuCl_4 and Cs_2CuBr_4 . These compounds exhibit a geometric structural change with no change in coordination number or spin-state and belong to class 2A.

(2) Five-coordinate complexes

An X-ray diffraction study [241] of the $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5 \text{H}_2\text{O}$ com-

plex has shown that its unit cell contains two crystallographically independent $[\text{Ni}(\text{CN})_5]^{3-}$ ions, one with a regular square-pyramidal geometry, and one with a distorted trigonal-bipyramidal geometry. Dehydration of the complex converts all of the $[\text{Ni}(\text{CN})_5]^{3-}$ ions to the square-pyramidal geometry [241]. When this compound was subjected to pressures of ca. 7 kbar at 78 K, the coordination geometry of the trigonal-bipyramidal $[\text{Ni}(\text{CN})_5]^{3-}$ ion was converted reversibly to the square-pyramidal geometry [231]. The IR spectrum of this compound at ambient and high pressure is presented in Fig. 17. In order to prevent the dehydration of the complex at high pressure (presumably a result of localized heating produced by the 6X beam condenser used with the pressure cell) these studies were made at 78 K. In this complex, the reversible transformation represents behavior class 2A in a five-coordinate complex.

An extensive high-pressure study of many five-coordinate nickel(II) complexes with ligands ranging from monodentate to tetradentate has revealed several nonrigid structures in the solid state [223]. The results for several metal ions are presented in Table 25 and reveal that "tripod-like" tetradentate ligands prefer the trigonal-bipyramidal structure. The importance of the larger number of chelate rings, and the increased entropy and free energy of formation for tetradentate ligand complexes of the type $[\text{NiLX}]_2\text{Y}$, are indicated by the more numerous trigonal-bipyramidal structures. As the number of chelate rings is reduced, stability decreases, and the tendency to form intermediate five-coordinate complexes results [242]. NiL_3X_2 complexes with no chelate rings are unstable and dissociate in solution, whereas the application of high pressures tends to distort these solids toward the distorted intermediate five-coordinate geometry. In these five-coordinate complexes, a gradual change from class 1 behavior (with small values of $d\nu/dp$) to class 2A behavior is observed.

The five-coordinate square-pyramidal complex $\text{Fe}(\text{NO})(\text{salen})$ ($\text{salen} = \text{N,N}'$ -ethylenebis(salicylideneimine)) has been shown to contain iron in an intermediate spin state ($S = \frac{3}{2}$) and to exhibit spin equilibrium at low temperature [243]. Mössbauer spectral results indicate that the complex most likely contains $\text{Fe}(\text{III})$ and NO^- , although this formulation is still open to question. A recent study of the NO vibrational absorption band as a function of pressure has revealed a shift to lower frequency at high pressure [244]. These results appear to be consistent with a change in spin state for the iron ion. This compound would appear to fit into class 3, but additional studies will be required to confirm and refine this classification because structural changes may also be significant.

Two isomers of $\text{Co}(\text{NO})(\text{Ph}_2\text{CH}_2\text{P})_2\text{Cl}_2$ are known [245]. One of these isomers is trigonal bipyramidal and contains $\text{Co}(\text{I})$ and NO^+ ions, most probably with a linear $\text{Co}-\text{N}-\text{O}$ bond. The second isomer is square pyramidal and contains $\text{Co}(\text{III})$ and NO^- with a bent $\text{Co}-\text{N}-\text{O}$ bond. The NO vibrational absorption band occurs at ca. 1750 cm^{-1} in the first isomer and at ca. 1650 cm^{-1} in the second. A preliminary study indicates the structural conversion of the trigonal-bipyramidal isomer to the square-pyramidal isomer at high pressure

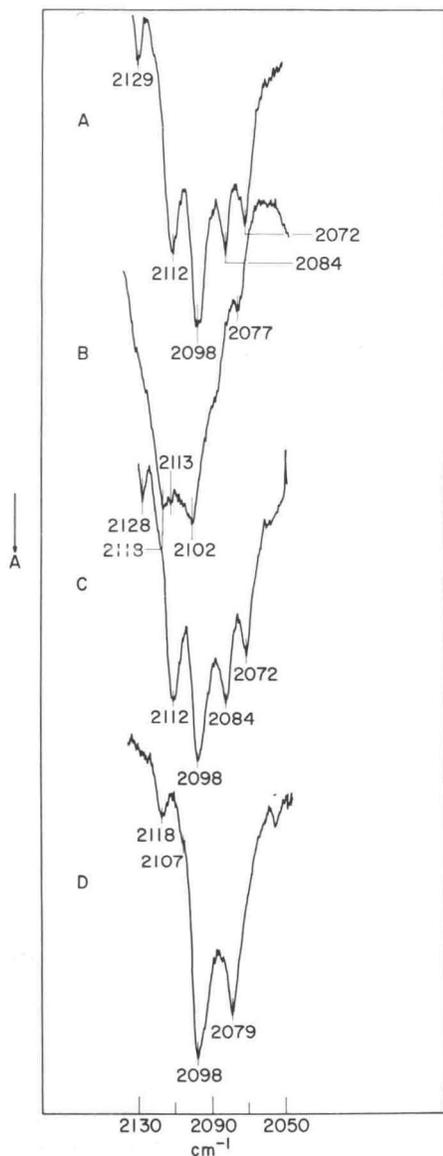


Fig. 17. The cyanide stretching vibrational bands in $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5 \text{H}_2\text{O}$: A, at 78 K and ambient pressure; B, at 78 K and ca. 7 kbar; C, at 78 K and ambient pressure after release of high pressure. Spectrum D is that of $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5]$ at ambient temperature and pressure [249]. (Figure reproduced through the courtesy of the authors and the American Chemical Society, Washington, D.C.)

TABLE 25

Structural inferences from pressure effects for several Ni(II), Pd(II), Pt(II) and Co(II) complexes containing ligands varying from tetradentate to monodentate [223]

Complex ^a	Type of ligand	$d\nu/dp$ ($\text{cm}^{-1} \text{ kbar}^{-1}$)	Structure
[NiLX]Y (24)	Tetradentate	33-70	TBP
[PdLX]Y (2)	Tetradentate	33-81	TBP
[PtLX]Y (1)	Tetradentate	27	TBP
[CoLX]Y (1)	Tetradentate	7	SQP
[NiLX ₂] (3)	Tridentate	9-32	Distorted, TBP-SQP
[NiL ₂ X]Y (5)	Bidentate	9-32	Distorted, TBP-SQP
[CoL ₂ X] (2)	Bidentate	Very slight shift	SQP
[NiL ₃ X ₂] (6)	Monodentate	8-29	Distorted, TBP-SQP
[CoL ₃ X ₂] (2)	Monodentate	8-23	Distorted, TBP-SQP

^a Numbers in parentheses indicate number of compounds studied.

Abbreviations: TBP = trigonal bipyramid; X = halide or pseudo-halide ion; SQP = square pyramid; Y = polyatomic anion.

[236]. This represents class 4 behavior with significant structural and electronic changes.

(3) Six-coordinate complexes

To date we have not been successful in changing the coordination number or geometry of an octahedral (or close to octahedral) complex at high pressure. However, several octahedral high-spin complexes have been reversibly converted, at least in part, to the analogous low-spin octahedral complexes at high pressure [215,216,246,247]. Table 22 summarizes some of these results. The initial conversion from the high-spin to the low-spin state has been explained [27,216] by the increase in ligand-field potential with pressure until it exceeds the electron pairing energy. This initial effect is accompanied by the back-donation of the metal t_{2g} electrons into the π^* orbitals of the ligand. With a further increase in pressure this back donation is reduced by the accessibility of π electrons from the ligand [27].

(4) Nonrigidity of solids at high pressure

It may be concluded that solid-state high-pressure structural transformations are possible in transition-metal complexes. All of the transformations examined thus far have been reversible, with the exception of that in Ni-(Qnqn)Cl₂, in which a dimer is formed at high pressure. In this complex, two additional bonds are formed on dimerization, and they contribute to the stability of the high-pressure phase.

The probability of producing structural interconversions with pure or nearly pure tetrahedral and octahedral complexes is predicted, on the basis

of the theoretical considerations discussed [197,198], to be small. For undistorted tetrahedral complexes, this prediction is borne out by experiment. Attempts [248] to convert complexes of nearly tetrahedral symmetry have been unsuccessful. The results of our work, however, indicate that the pressure-induced conversions of tetragonally distorted tetrahedral complexes are possible, in particular where an asymmetric ligand field is observed by the central atom (e.g., a complex involving several types of ligands). The importance of a distorted structure appears to be a necessity in a solid-state pressure conversion [249].

It is possible that distorted six-coordinate complexes may also behave similarly [250–252]. The results observed to date for four- and six-coordinate complexes are not surprising because the energy barrier to rearrangement for true tetrahedral and octahedral structures is certainly high. For the $\text{Ni}(\text{BzPh}_2\text{P})_2\text{Br}_2$ complex, the unpaired electrons may contribute to the lowering of the energy difference between the distorted tetrahedral and the square-planar configurations. This effect would be superimposed upon the beneficial effect of a starting structure which is distorted toward the square-planar geometry.

For five-coordinate complexes the energy barrier for structural interconversion is small, and many examples have been reported in which the trigonal-bipyramidal and square-pyramidal isomers both exist [246,253–257]. This is apparently also true in the solid state, because our high-pressure studies indicate that interconversion is readily obtained. In systems containing a tripod-like tetradentate ligand, the ligand flexibility favors the trigonal-bipyramidal structure. For the $\text{Ni}(\text{CN})_5^{3-}$ ion, a structure which is distorted in the direction of the pressure-stable square-pyramidal phase, the monodentate cyanide ion permits the rearrangement to occur.

Nonrigid configurations for seven- and eight-coordinate complexes have been demonstrated in solution studies [258–269]. However, no solid-state high-pressure studies have been reported to date.

Recent studies have disclosed pressure effects on solids which are interesting and surprising [270,271]. Copper(II) and nickel(II) complexes of *N,N*-diethylethylenediamine, *N,N*-dimethylethylenediamine and *C,C*-dimethylethylenediamine of the type $\text{M}(\text{L})_2\text{X}_2$ where X = anion, have been found to be reversibly thermochromic [271a]. The Lever effect has been advocated as the mechanism for the thermochromism, axial interactions between the anions and the $\text{M}-\text{N}_4$ plane increase with temperature and metal–nitrogen distances are expanded. Axial interaction causes an increase in coordination number from 4 to 6, accompanied by a color change. The reverse occurs with an increase in pressure, and axial interactions are at a minimum, maintaining the four-coordinate state.

A pressure study involving MCl_4^{2-} ions was made using counter ions which were capable of hydrogen bonding and those which were incapable [272]. It was found that hydrogen bonding stabilizes an octahedral geometry for Mn^{2+} and Fe^{2+} . With Ni^{2+} , preparations in solution gave RNiCl_3 complexes which

TABLE 26

Summary of pressure effects on R_2MCl_4 complexes [272]

Counterion ^b	Mn(II) d^5	Fe(II) d^6	Co(II) d^7	Ni(II) d^8	Cu(II) d^9
R_4N^+	T_d	T_d	T_d	T_d	D_{2d}
R_3NH^+	Increasing internal pressure				
$R_2NH_2^+$					
RNH_3^+	O_h	O_h	D_{2d}	O_h^a	D_2 and D_{2h}
R_3NH^+	Increasing internal pressure				
$R_2NH_2^+$					
RNH_3^+			D_{2d}		D_{2h}

^a Stoichiometry involves $NiCl_3^-$ from solution; from melt [272] polymeric octahedral structures are obtained with a stoichiometry of $[R_2NiCl_4]_x$. ^b R = alkyl group.

contain $NiCl_6$ octahedra, and polymeric octahedral complexes with the stoichiometry $(R_2NiCl_4)_x$ from melts. Table 26 summarizes the results of pressure effects on R_2MCl_4 complexes.

F. GEOLOGICAL APPLICATIONS

The interior of the earth is at high temperature and under megabar pressures. In our discussions heretofore we have stressed changes in molecules created at kbar pressures. It is of the utmost importance to be able to know what major physical and chemical changes occur to matter at megabar pressures. Since the composition of the core and the mantle involve, besides silicates, transition metal minerals, mostly iron and nickel, effects of Mbar pressures and high temperatures on these substances is of obvious interest. It would be expected that transition chemistry under these conditions would be different than under ambient conditions. Changes in oxidation state, spin state, coordination numbers, and absorption properties with pressure and temperatures affect the density, magnetic, electrical and thermal properties of the earth's interior. It is of interest to geochemists and to geophysicists to simulate conditions in the laboratory to make p and t studies on minerals. New concepts of the earth's constitution, evolution and properties depend on these studies, and the interpretation of the results. This research would serve to answer many questions which still remain unanswered concerning our own planet, and could serve as an aid in explaining the behavior of other planets. Studies at high temperature and Mbar pressures are now possible, and have commenced. The necessary experimental tools to accomplish this are now available (see Section B). X-ray, Mössbauer and visible measurements have been made with the Mbar cell of Mao and Bell [289,297,303]. Vibrational spectroscopy may play a role in these applications in the future. However, the present construction of the cell may restrict its use in the IR region, because

of the severe energy requirements and the need to accommodate a beam condenser [273]. However, it is possible that new instrumentation involving tunable diode lasers in the IR may overcome these difficulties.

Many of the original studies to attempt to create Mbar pressures were done with shock waves [274]. As previously stated, this is a rather difficult and destructive way to study the problem. Modern techniques using the diamond anvil cell to Mbar pressures and 3000°C are now available, and this should provide impetus to this field.

Table 27 shows some examples of early general results or effects of t and p (50 kbar or less) on minerals. Transformation of minerals with t and p indicate that few minerals found on the surface would be stable in the deep interior of the earth, an observation made by Bridgman in 1945.

The effects of t and p on interatomic distances in oxygen-based minerals have been reported [298,299]. Mechanisms of Si(IV) to Si(VI) in silicate minerals have also been determined [300]. Other mineral studies have also appeared recently in the literature [301,302].

Some more recent studies of minerals at higher pressure are outlined in Table 28. Ming and Bassett [296] have found from their t and p studies that at 250 kbar and 1000°C ferromagnesium silicate breaks down to the simple oxides of iron, magnesium and silicon. In the interior of the earth, below 650 km, it is believed that these oxides constitute the main mineral constituents in the mantle. The presence of iron oxides is of considerable interest since they play a major role in determining the optical, electrical and thermal properties of the mantle as well as in the evolution of the earth.

An interesting result of studies at high pressure and temperature were those of Bell et al. [297]. Studying iron-rich basaltic glass at 100–150 kbar and ca. 2000°C they showed that the ferrous-bearing compounds would disproportionate into a ferric iron phase plus a metallic iron phase. Thus, both a highly oxidized crust and a metallic core can coexist and can be simultaneously formed, obviating some early evolutionary history of earth. The results lend support to the fact that the core and mantle may exist in a chemical equilibrium.

TABLE 27

Some mineral transformations at relatively low pressures

	Temp. (°C)	Pressure (kbar)	Ref.
β -Quartz \Rightarrow α -quartz	573– 800	24	275
α -Quartz \Rightarrow coesite	400– 600	10	276, 277
	700–1700	20	278
Sillimanite \Rightarrow kyanite	1000–1500	5	279, 280
Albite \Rightarrow jadeite + quartz	600–1000	50	281
Fayalite \Rightarrow spinel		25	282, 283

TABLE 28

Transformation of several minerals at high temperatures and pressures [296]

Mineral	Pressure (kbar)	Temp. (°C)	Products	Ref.
FeSiO ₃ , ferrosilite	95	1000	Fe ₂ SO ₄ + SiO ₂ , stishovite	284
(Fe, Mg)SiO ₃ , clinopyroxene	80–180	1000	(Fe, Mg) ₂ SiO ₄ , spinel + SiO ₂ , stishovite	285, 286
MgSiO ₃ , clinoenstatite	200–280	1000	Mg ₂ SiO ₄ , β-phase + SiO ₂ stishovite	287
β-Mg ₂ SiO ₄	>280	1000	γ-Mg ₂ SiO ₄ , spinel	287
Fe ₂ SiO ₄ , spinel	250	1000	FeO + SiO ₂ , stishovite	288, 289
(Mg, Fe) ₂ SiO ₄ , olivines	50–150	1000	Spinel, γ-phase	290–294
Mg ₂ SiO ₄ , fosterite	330	1000	MgO + SiO ₂ , stishovite	295
Complex basalt	100–150	2000	Fe ₂ O ₃ + Fe	297

Minerals containing iron, such as olivine and spinel, under pressure, appear to indicate that a marked increase in conductivity occurs with pressure in excess of 100 kbar [303]. Similar results have been indicated with other solid phases approaching metallic behavior with pressure. In addition, charge transfer properties change in these minerals due to pressure effects on electronic orbitals [286]. These effects bear heavily on the earth's internal temperature and electrical conductivity, as well as on models of earth formulated to date. The question of whether the thermal conductivity in earth is radiative or conductive may, in part, have been answered in the Bell et al. [297] experiment. Both iron and ferric oxides are opaque to thermal radiation, but have high thermal conductivities.

We have only attempted to briefly indicate some geological applications of T and P. Further discussions are available in several reviews [274,303,304], and other reports [305–307].

G. SUMMARY

A summary of the solid state pressure effects discussed in the previous sections follows.

(i) Structural transformations

We have discussed a number of structural transformations that occur in the solid state under pressure. These are summarized below. (1) Phase changes in alkali metal halides, rare earth monochalcogenides from NaCl to CsCl structure where C.N. 6 → 8. (2) Transitions occurring in minerals where C.N. 4 → 6. (3) Transitions to metallic state, e.g., rare earth monochalcogenides, iodine,

solid hydrogen, xenon. (4) Transformations in coordination compounds. The various types of transformations are listed in Table 24. It may be noted that some structural changes occur with an increase in coordination number, and others occur with no change.

(ii) Effects on vibrational transitions

Four types of pressure-sensitivity for molecular vibrations have been observed thus far in the course of pressure studies on various modes of vibrations: (1) a broadening and a decrease in peak intensity of vibrations; (2) the doubling of absorption bands; (3) the splitting of degenerate vibrations; (4) frequency shifts in bands. Some of these effects have been observed for both external and internal vibrations.

(1) External vibrations

The effects of pressure on external vibrations have been demonstrated. Both the longitudinal and transverse optical modes are seen to shift in compressible ionic solids. In all cases studied thusfar, the shift is in the direction of higher frequency in agreement with low-temperature shifts. However, the pressure shifts may be considerable when compared with the temperature shifts. It is known that the temperature dependence of the peak position and half-width of lattice vibrational modes consist of two contributions: (1) the purely volume-dependent contribution; and (2) the contribution from the various anharmonic (cubic and higher) terms in the potential energy of the lattice. Often the directions of shifts in the temperature dependence experiment may be opposite to each other, resulting in a cancellation, and a small overall shift. For example, the specific volume of α -quartz shows only a 0.3% decrease from room to liquid-air temperatures [308], and this is smaller than the change occurring upon compression from ambient pressure to 4 kbar [309]. Such pressure studies may provide useful information on the amount of anharmonicity existing in solids of this type. Further, it should be possible in some cases to obtain compressibility data in compressible solids from pressure-frequency measurements (see eqn. (1)). Molecular lattices show similar pressure effects [79].

In addition to the spectral blue shifts, lattice vibrations will broaden and diminish in peak intensity. This appears to be characteristic of all types of vibrations. No quantitative studies have been made to determine the effect of pressure on the integrated intensities of these vibrations. This may prove to be very difficult, since results may not be reproducible because of the pressure gradient existing across the diamond anvil faces. The broadening effects may be connected in part with this pressure gradient, since Raman studies in a hydrostatic cell do not show this pressure broadening of lattice bands [79,159].

The blue shifts of ionic or molecular lattice modes may result from the contraction of the solid under pressure, causing interionic and intermolecular

distances to shorten [48,167,310,311]. The large pressure effects on compressible lattices are related to the small repulsive forces present in the neighboring ions or molecules.

(2) Internal vibrations

Earlier work indicated that internal modes are affected by pressure, but in a much less dramatic way than the external modes. Frequency shifts are generally small in most cases, either in a blue or red direction. In hydrogen-bonded compounds, studies of the O—H stretching vibration indicated spectral red shifts [48,310]. Red shifts were also observed for HgCl_2 and its dioxane complex by Mikawa et al. [145]. In most of our pressure studies with internal modes, blue shifts have been observed.

The broadening of bands and decreased peak intensities also occur with pressure. In some cases the symmetrical stretching vibration (A_1 species) is found to be particularly sensitive to pressure [203]. This compares favorably with the findings of Nedungadi [312], who studied the temperature dependence of α -quartz and found that the most sensitive vibration was an A_1 -type mode. Pressure dependencies of α -quartz produced similar results with the A_1 frequencies more sensitive than the E -type vibration [313]. Again, it must be inferred that not all A_1 vibrations are pressure sensitive, as A_1 bending vibrations and certain A_1 stretching vibrations are not particularly affected at higher frequencies.

Other pressure effects have recently been demonstrated. The $\nu_4(F)$ bending vibration in KMnO_4 , which is already split into two bands at ambient conditions, proceeds to lose all of its degeneracy with pressure. Studies with ligand ring vibrations in the mid-IR region have demonstrated that one can also obtain a doubling of vibrations with pressure [199]. An attempt to explain these results, at least qualitatively, follows.

(a) *Sensitivity of ν_1 stretching vibration to pressure.* The sensitivity of the ν_1 stretching vibration in various compounds (inorganic and coordination compounds) is especially interesting. By contrast, a symmetrical bending vibration of type A_1 may not be particularly affected (Fig. 16 illustrates the sensitivity of the A_1 species in the metal—chloride stretching region). The intensity of the symmetrical stretch has practically disappeared with pressure, while the asymmetric stretch, although less intense, is still readily observed.

This ν_1 vibration involves an expansion of molecular volume, and these "expansion vibrations" are particularly sensitive to pressure [203]. In addition, the dipole moment change for the vibration apparently decreases and this causes a decrease in the intensity. The actual mechanism as to how this is accomplished is obviously unknown at present. Since the intermolecular distances are being diminished, it may be possible to change certain bond angles while the material is under external stress. If the bond angles increase and approach 180° , the dipole moment change for the vibration might approach zero. Carbon dioxide is a case in point, where the bond angle

O—C—O is 180° and the ν_1 vibration is forbidden in the IR spectrum. However, it is observed in the Raman measurements and it would be interesting to observe similar molecules in the Raman experiment with pressure. Water, with a bond angle of ca. 104° , shows an IR-active ν_1 vibration.

(b) *Splitting of degenerate vibrations.* The loss of the degeneracy of E or F type vibrations with pressure is possible. In some cases this may be due to a lowering of symmetry of the molecule. In other cases, where a molecule may have two or more molecules per unit cell, it is possible that the vibrations in the unit cell might couple, causing a factor group splitting (Davydov splitting) [314].

(c) *Doubling of absorption bands.* In the course of various studies [199] it has been observed that a doubling of bands occurs with pressure. This may be due to a lowered site symmetry induced in the solid state by the external pressure. Alternatively, two accidentally overlapping vibrations may occur at the same frequency. These may be induced to separate because of a difference in the pressure dependencies manifested by the two vibrations. Alternatively, this may be caused by factor group splitting.

(d) *Lack of frequency shift for internal modes.* The lack of large frequency shifts for most internal modes in polyatomic compounds is a very useful consequence, for it may allow one to distinguish between such a vibration and a lattice mode in a compressible solid. The lack of larger shifts is related to the stronger repulsive forces present in the atoms of these molecules. However, it is dangerous to extrapolate that all internal modes will behave in this manner. The electron density around the various atoms involved may be a very important factor. As the pressure is increased and the atoms or molecules approach each other, the interaction of the electron field increases. For simpler molecules with minimal electronic interaction, such as hydrogen, it may be possible for considerable shifts in frequencies of the internal mode to occur; however, as the electronic fields become more and more complex, the repulsive forces increase and the shifts decrease. Vu et al. [315] demonstrated that a shift of ca. $1 \text{ cm}^{-1} \text{ kbar}^{-1}$ occurs for the pressure-induced $\nu_{\text{H-H}}$ vibration in solid hydrogen. A somewhat lower pressure dependence is found for HCl [316].

(iii) *Functional approach to explain pressure effects*

Recently, Gutmann and Mayer [317] have attempted to explain pressure effects on materials using the functional approach. This is based on a model which considers that pressure acts by increasing the electron donor properties of parts of the systems. In many ways pressure may be considered to play the role of an electron donor. In this way, some of the pressure effects on molecules may be explained.

H. MISCELLANEOUS

Several new pressure conversions of gases to a metallic state are possible in view of existing high-pressure instrumentation. For a discussion on metallic hydrogen, see refs. 318–323. For the possible conversion of xenon to a metallic state, see Ruoff and Nelson [324]. Many of the aforementioned physical tools used with the DAC, including electronic and vibrational spectroscopy, may play a role in the analyses and characterization of these possible new metallic phases.

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