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Effect of Pressure on Crystal-Field Energy and Covalency in Octahedral Complexes of Ni^{2+}, Co^{2+}, and Mn^{2+} †

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The effect of pressure has been measured on the absorption spectra of $NiCl_2$, $NiBr_2$, $Ni(NH_3)_6Cl_2$, $CoCl_2$, $CoBr_2$, $MnCl_2$, and $MnBr_2$. The pressure shifts in every case correspond to increase in crystal field strength. To account for the shifts in a quantitative manner it is necessary to presume that the Racah parameter B decreases with increasing pressure. This can be interpreted as an increase in covalency at high pressure.

From the data on $MnCl_2$ and $MnBr_2$ it is possible to establish limitations on the possible range of values of the parameter ϵ introduced by Koide and Pryce to describe covalency in transition metal complexes.

THE effect of pressure has been measured on the optical absorption spectra of the chlorides and bromides of Ni^{2+}, Co^{2+}, and Mn^{2+}, as well as on $Ni(NH_3)_6Cl_2$. The types and sources of experimental material are summarized in Table I. The high-pressure optical techniques have been described elsewhere.[1,2]

The peaks which were observed are listed in Table II, in the abbreviated nomenclature used in this paper together with their normal assignments in group theoretical nomenclature. As will be discussed below, the assignment of the peak for Co-III can be made with considerable assurance based on the pressure shift. Peak III-Mn is really two transitions having the same crystal field energy, as discussed in a later section of the paper. The measurements on the high-energy peaks of $CoBr_2$ and $NiBr_2$ were limited by the red shift of the charge transfer peak.

Tanabe and Sugano[3] have developed equations for the energy of the transitions; as a function of the crystal field strength 10 Dq, and of the Racah parameters B and C.

For Ni^{++} the equations for the three transitions are

$$E(\text{I}-\text{Ni})=10Dq \tag{1}$$

$$E(\text{II}-\text{Ni})=15Dq+7.5B-6B[1+\mu]^{\frac{1}{2}} \tag{2}$$

$$E(\text{III}-\text{Ni})=15Dq+7.5B+6B[1+\mu]^{\frac{1}{2}}, \tag{3}$$

where

$$\mu=(10Dq-9B^2)/12B.$$

For all values of the parameters Dq and B in the range studied $\mu\ll1$.

For Co^{++} the equations for the transitions studied are

$$E(\text{I}-\text{Co})=5Dq-7.5B+6B(1+\eta)^{\frac{1}{2}} \tag{4}$$

$$E(\text{II}-\text{Co})=15Dq-7.5B+6B(1+\eta)^{\frac{1}{2}} \tag{5}$$

$$E(\text{III}-\text{Co})=12B(1+\mu)^{\frac{1}{2}}$$

$$\eta=[(10Dq+9B)/12B]^2. \tag{6}$$

For Mn^{++} the energies of the transitions can be obtained from the following equations:

$$\begin{vmatrix} -10Dq+10B+6C-E & -(18)^{\frac{1}{2}}B & \mathrm{C} \\ -(18)^{\frac{1}{2}}B & 9B+C-E & -18B \\ C & -(18)^{\frac{1}{2}}B & 10Dq+18B+6C-E \end{vmatrix}=0, \tag{7}$$

where the lowest root $E=\text{I}-\text{Mn}$;

$$\begin{vmatrix} -10Dq+18B+6C-E & 6^{\frac{1}{2}}B & 4B+3 \\ 6^{\frac{1}{2}}C & 13B+5C-E & -6^{\frac{1}{2}}B \\ 4B+C & -6^{\frac{1}{2}}B & 10Dq+18B+6C-E \end{vmatrix}=0, \tag{8}$$

where the lowest root $E=\text{II-Mn}$; the second lowest root $E=\text{IV-Mn}$.

$$E(\text{III-Mn})=10B+5C \tag{9}$$

$$E(\text{V-Mn})=17B+5C. \tag{10}$$

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[1] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. **47**, 1015 (1957).

[2] H. G. Drickamer, Rev. Sci. Instr. **32**, 212 (1961).

[3] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753, 766 (1954).

TABLE I. Materials investigated.

Compound	State investigated	Source or method of preparation
$NiCl_2$ $NiBr_2$	powder or approximately equal mixture of material and NaCl in powder form	Preparation from metal acetate hydrate and acetyl halide reagent-grade chemicals used.
$CoCl_2$ $CoBr_2$		
$MnCl_2$ $MnBr_2$	single crystal	R. Pappalardo, Bell Telephone Laboratories
$Ni(NH_3)_6Cl_2$	approx equal powder mixture with NaCl	Material prepared from $NiCl_2(H_2O)_6$ and ammonia using reagent grade chemicals

DISCUSSION

In the simplest crystal field theory one should be able to predict the energies of each transition from the crystal field strength Dq and the free ion value of B (or of B and C). This is almost never possible. It is frequently possible to establish a value of B and Dq which will fit all the peaks at atmospheric pressure. Table III shows these values (labeled Dq_0 and B_0) for Co^{++} and Ni^{++}.

It seems reasonable to assign the decrease in the value of B going from free ion to crystal to a spreading out of the metal ion charge cloud because of covalent interaction with the ligands. Another approach to covalency has been proposed by Koide and Pryce.[4] They presume that the d_ϵ orbitals which point at the ligands are involved in covalent interaction while the d_t orbitals are unaffected. Their formulation has been applied to Mn^{++} by Pappalardo[5] and by Stout[6] as well as the original authors. We have extended it also to Ni^{++}.

The effect of pressure on the crystal field and ionic parameters is discussed in the following paragraphs. Emphasis is placed on those factors which are relatively independent of the atmospheric pressure values of the Racah parameters as these are not well established. For each metal ion we discuss the change in crystal field strength assuming B is constant and equal to B_0; then the change in B (or B and C) with pressure is considered. In the final section of the paper we discuss the Koide and Pryce parameter ϵ.

TABLE II. Nomenclature for electronic transitions.

Nomenclature (this work)		Standard nomenclature
Absorption peak		
Ni^{++}		
	I	${}^3A_2(F)\rightarrow{}^3T_2(F)$
	II	${}^3A_2(F)\rightarrow{}^3T_1(F)$
	III	${}^3A_2(F)\rightarrow{}^3T_1(P)$
Co^{++}		
	I	${}^4T_1(F)\rightarrow{}^4T_2(F)$
	II	${}^4T_1(F)\rightarrow{}^4A_2(F)$
	III	${}^4T_1(F)\rightarrow{}^4T_1(P)$
Mn^{++}		
	I	${}^6A_1(S)\rightarrow{}^4T_1(G)$
	II	${}^6A_1(S)\rightarrow{}^4T_2(G)$
	IIIa	${}^6A_1(S)\rightarrow{}^4A_1(G)$
	IIIb	${}^6A_1(S)\rightarrow{}^4E_g(G)$
	IV	${}^4A_1(S)\rightarrow{}^4T_2(D)$
	V	${}^4A_1(S)\rightarrow{}^4E_g(D)$

CHANGES OF *Dq* AND *B*

Equations (1)–(3) predict that, if the Racah parameter B is constant, peaks I-Ni, II-Ni, and III-Ni should show a large increase in energy (blue shift) with increasing crystal field strength (increasing pressure).

TABLE III. Atmospheric values of the parameters and peak energies used to determine them.

Material	B (free ion)	1 atm value in solids B_0	Dq_0
$Ni(NH_3)_6Cl_2$	1030	887	1090
$NiCl_2$	1030	823	755
$NiBr_2$	1030	730	728
$CoCl_2$	971	766	750
$CoBr_2$	971	713	697

	Absorption peaks[a]					
	Peak I $10^3\ cm^{-1}$		Peak II $10^3\ cm^{-1}$		Peak III $10^3\ cm^{-1}$	
	A	B	A	B	A	B
$Ni(NH_3)_6Cl_2$	10.9	10.9	17.85	17.49	28.52	28.52
$NiCl_2$	7.55	7.55	12.56	12.5	22.57	22.57
$NiBr_2$	7.28	7.28	12.0	12.0		
$CoCl_2$	6.58	6.58			17.1	17.1
$CoBr_2$	6.09	6.09			15.9	15.9

[a] Column A, experimental; Column B, calculated using Dq_0 and B_0.

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[4] S. Koide and M. H. L. Pryce, Phil. Mag. **3,** 607 (1958).

[5] R. Pappalardo, J. Chem. Phys. **31,** 1050 (1959); **33,** 613 (1960).

[6] J. W. Stout, J. Chem. Phys. **31,** 709 (1959); **33,** 303 (1960).

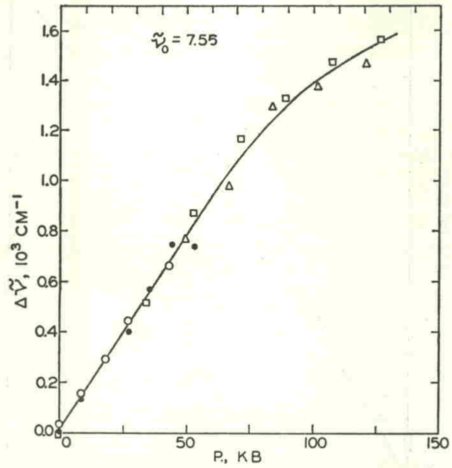

FIG 1. Pressure shift for I-Ni peak in $NiCl_2$.

Peaks II-Ni and III-Ni should shift roughly $1\frac{1}{2}$ times as fast as peak I-Ni. The experimental data for Ni^{++} are shown as the points and solid lines in Fig. 1-8. It can be seen that the data are in qualitative agreement with experiment. Since peak I-Ni depends on *Dq* only, it should be possible to predict the shifts of peaks II-Ni and III-Ni from peak I-N and B_0. The dotted lines in Fig. 2, 3, 5, 7, and 8 represent this calculation. The discrepancies are certainly larger than possible experimental error. The deviation is larger for peak III-Ni than for peak II-Ni. Since III-Ni is relatively sensitive to the value of *B* while II-Ni is quite insensitive, it would appear that *B* is decreasing with increasing pressure. It is possible to calculate meaningful values for *B* from peak III-Ni using *Dq* from peak I-Ni. Peak II-Ni is too insensitive to give significant values for *B*. The results for $NiCl_2$ and $Ni(NH_3)_6Cl_2$ are shown in Table IV together with results discussed below for $CoCl_2$, $MnCl_2$, and $MnBr_2$.

Within the accuracy of the data the calculated changes in *B* are of the same order for all complexes.

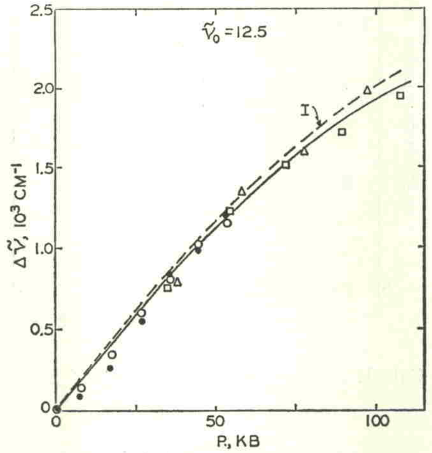

FIG. 2. Pressure shift for II-Ni peak in $NiCl_2$.

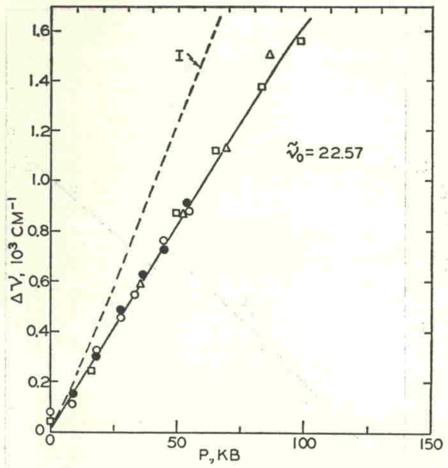

FIG. 3. Pressure shift for III-Ni peak in $NiCl_2$.

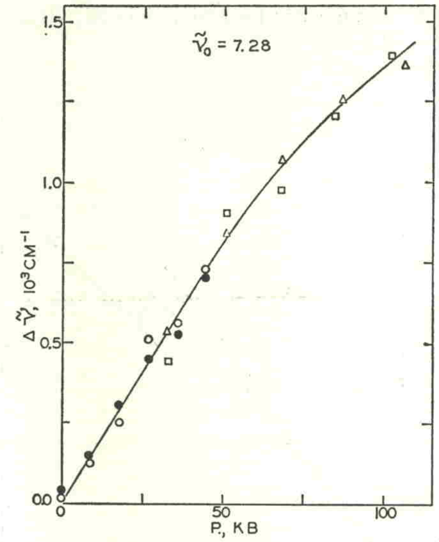

FIG. 4 Pressure shift for I-Ni peak in $NiBr_2$.

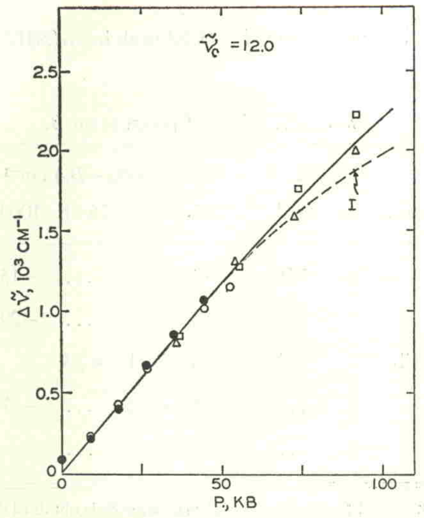

FIG. 5. Pressure shift for II-Ni peak in $NiBr_2$.

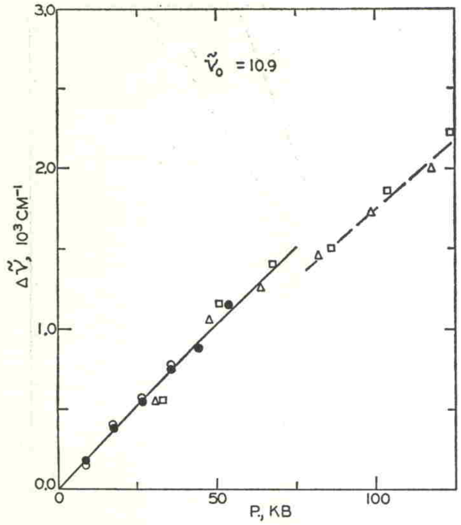

FIG. 6. Pressure shift for I-Ni peak in $Ni(NH_3)_6Cl_2$.

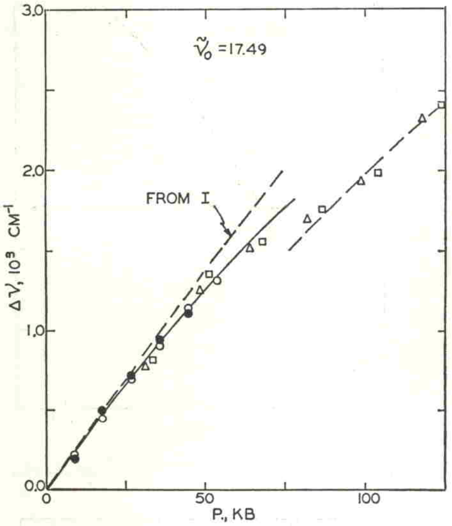

FIG. 7. Pressure shift for II-Ni peak in $Ni(NH_3)_6Cl_2$.

TABLE IV. Effect of pressure on B.

Substance	B_0 cm^{-1}	(B_P-B_0) cm^{-1} 25 kb	50 kb	75 kb	100 kb	150 kb
$CoCl_2$	766	−4	−8	...	−15	−21
$NiCl_2$	823	−4	−19	...	−29	
$Ni(NH_3)_6Cl_2$	887	−3	−11	−23		
$MnCl_2$	...[a]	−6	−12	...	−27.5	
$MnBr_2$	...[a]	−9	−18	...		

[a] B_0 is not needed for $MnCl_2$ and $MnBr_2$ as B_P-B_0 is obtained directly from the shifts.

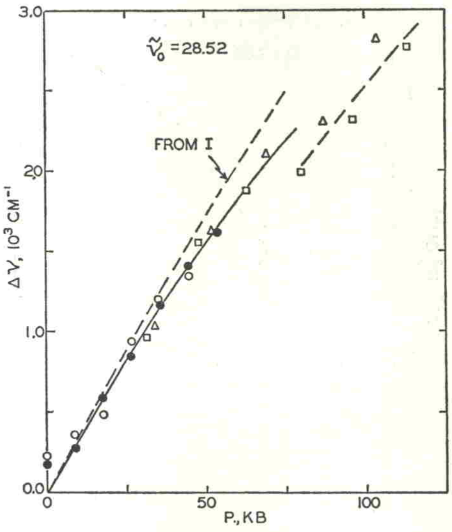

FIG. 8. Pressure shift for III-Ni peak in $Ni(NH_3)_6Cl_2$.

The $Ni(NH_3)_6Cl_2$ has a higher value of B_0 and shows a slightly smaller deviation of peak III when calculated for constant B. Just above 75 kbar there appears a small but consistent discontinuity in the shift for all three peaks of this compound. There also seemed to be some loss of light at this point. A first-order phase transition is possible, but cannot be proven.

It should be mentioned that our previous data on $Ni(NH_3)_6Cl_2$[7] indicated an increase of B with pressure. Since peak I was not obtained at that time the calculations were made from peaks II and III, which is not as accurate a procedure. Also, those data were among the first obtained on our optical apparatus, and the methods of operation and calculation were not well established.

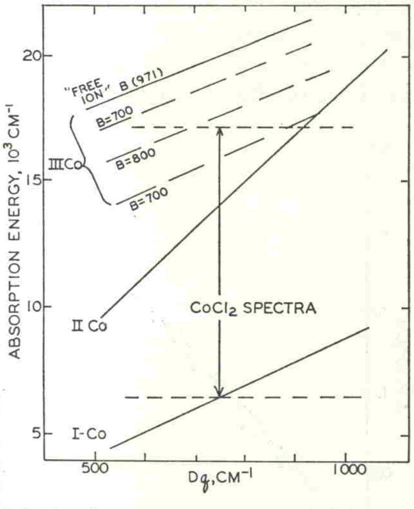

FIG. 9. Calculated energies for states in Co^{++} as a function of Dq and B.

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[7] R. W. Parsons and H. G. Drickamer, J. Chem. Phys. **29**, 930 (1958).

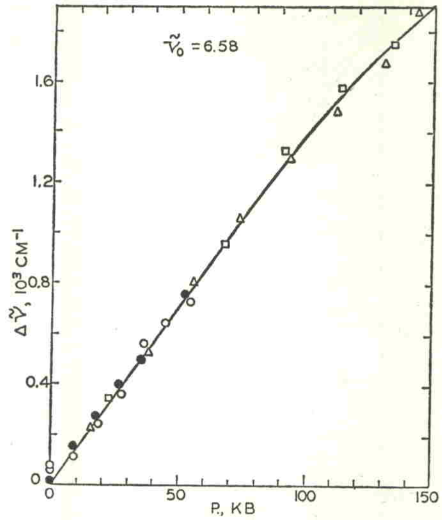

FIG. 10. Pressure shift for I-Co in $CoCl_2$.

Figure 9 shows the calculated change of energy of peaks I, II, and III for Co^{++} as a function of *Dq* and *B*. Peaks I and II are essentially independent of *B*, but peak III shows a definite *B* dependence. The solid lines and points in Figs. 10–13 show the measured shifts. Again large blue shifts are found, in qualitative agreement with theory. Fig. 14 shows the change in *Dq* with pressure as calculated from both peaks for $CoCl_2$. The dotted curves in Figs. 11 and 13 represent calculated shifts for peaks III-Co, using the value of *Dq* from peak I-Co and B_0. The discrepancies are larger than experimental error and can be represented as a decrease in *B* with pressure. The calculated decrease is shown for $CoCl_2$ in Table IV. It is of the same magnitude as that obtained for the Ni^{2+} complexes.

The dashed curve in Fig. 11 represents the calculated shift in this peak, if it is assigned to II-Co rather than III-Co. The discrepancy is clearly too large to be ac-

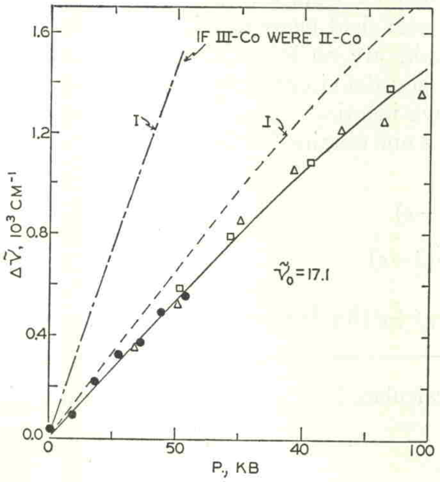

FIG. 11. Pressure shift for III-Co in $CoCl_2$.

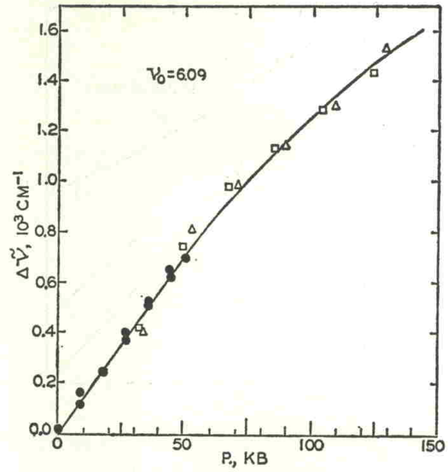

FIG. 12. Pressure shift for I-Co in $CoBr_2$.

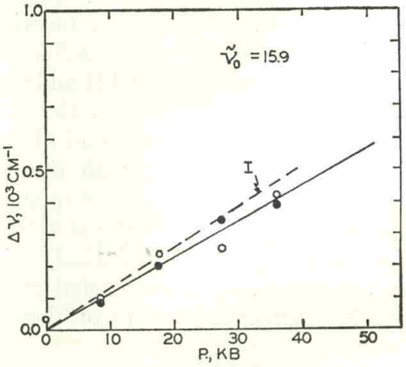

FIG. 13. Pressure shift for III-Co in $CoBr_2$.

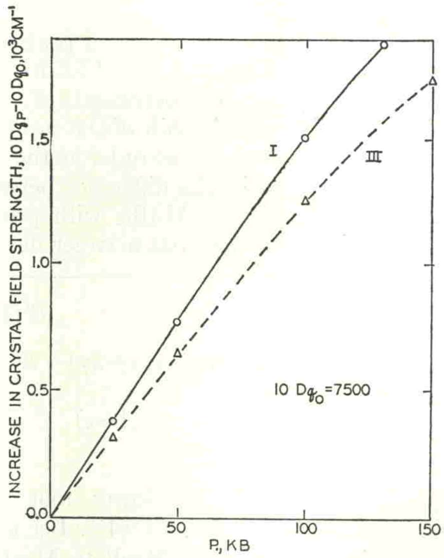

FIG. 14. Increase in crystal field strength with pressure—$CoCl_2$.

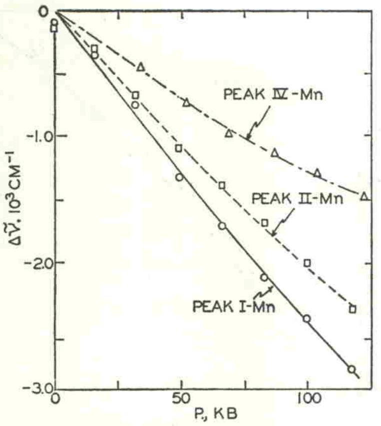

FIG. 15. Pressure shifts of peaks dependent on Dq in $MnCl_2$.

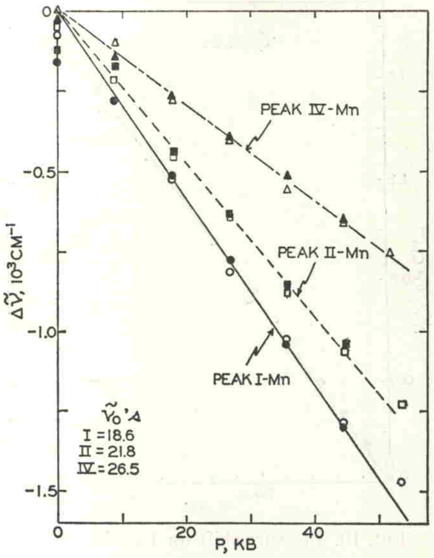

FIG. 16. Pressure shifts of peaks dependent on Dq in $MnBr_2$

counted for by any reasonable change in parameters and supports our assignment.

Equations (7) and (8) predict shifts for peaks Mn-I, Mn-II and Mn-IV which are complex functions of Dq, B, and C. For any reasonable values of B and C a large red shift is predicted for peaks I and II and a somewhat smaller red shift for peak IV. Figures 15 and 16 show the shifts of these peaks for $MnCl_2$ and $MnBr_2$. There is clearly qualitative agreement with theory. Unfortunately, the shifts are very sensitive to the absolute values of B and C, and the degree of quantitative agreement with experiment can be varied widely using values of these parameters within the accepted range at one atmosphere. No further discussion of these peaks is therefore offered.

From Eqs. (9) and (10) one can see that peaks III-Mn and V-Mn are independent of the crystal field energy, and should thus not shift with pressure if B and C are constant. Furthermore, the difference in energy of the two peaks equals $7B$.

Figures 17 and 18 show the shifts of peaks III-Mn and V-Mn with pressure for $MnCl_2$ and $MnBr_2$. Clearly B and C are not constant. The decrease in B, obtained directly from the difference in shift of the two peaks, is shown in Table IV. It is the same order as the changes for Ni^{++} and Co^{++}. While the difference between the change in B for $MnCl_2$ and $MnBr_2$ with pressure is rather small, it is reasonable that a larger decrease in B (greater increase in covalency) would be obtained with the more polarizable Br^- ion.

The change in the parameter C can be calculated from the equation

$$C_p-C_0=\frac{1.7(\text{shift for III}-\text{Mn})-\text{Shift for V}-\text{Mn}}{3.5}. \tag{11}$$

Figure 19 shows the decrease in B and C with pressure for $MnCl_2$ and $MnBr_2$. For values of $\gamma=C/B$ from 3–5 (the usual range postulated from atmospheric and free ion data) there would be a small increase in γ with increasing pressure.

ϵ AS A PRESSURE VARIABLE

From the pressure shifts of peaks Mn-III and Mn-V it is possible to obtain some useful results concerning the parameter ϵ. Peak III is really two peaks having the same crystal field energy. With the introduction of ϵ these peaks are no longer degenerate. In $MnCl_2$ and $MnBr_2$ they definitely appear as a doublet, but both peaks give identical shifts. Using Pappalardo's energy equations one obtains for these peaks

$$E'(\text{IIIa})=(10+5\gamma)(1-\epsilon) \tag{12}$$

$$\begin{vmatrix} 13+5\gamma-\epsilon(4+2\gamma)-E' & -2\sqrt{3}(1-\epsilon) \\ -2\sqrt{3}(1-\epsilon) & 14+5\gamma-\epsilon(22+7\gamma)+\epsilon^2(8+2\gamma)-E' \end{vmatrix}=0, \tag{13}$$

where $\gamma=C/B$, $E'=E/B$, the lower root of $E'=E'(\text{IIIb})$, and the second root $=E'(V)$. Let us define R as the relative shift of peak Mn-V to Mn-III with pressure. From the experimental data $R=1.25$ in the 50-kbar region, both for $MnCl_2$ and $MnBr_2$.

The calculated value of R (for constant γ) is

$$R=\frac{\partial E'(\text{V})}{\partial\epsilon}\bigg/\frac{\partial E'(\text{III})}{\partial\epsilon}. \tag{14}$$

Here, for E' (III) one can use E' (IIIa), E' (IIIb)

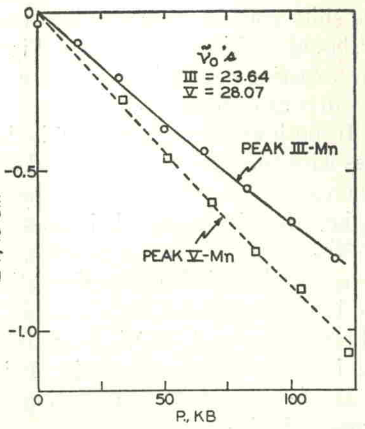

FIG. 17. Pressure shifts for peaks independent of *Dq* in $MnCl_2$.

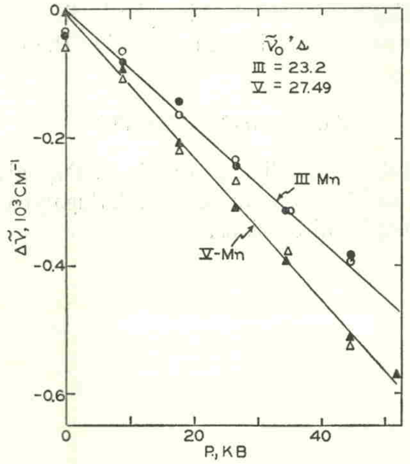

FIG. 18. Pressure shifts for peaks independent of *Dq* in $MnBr_2$.

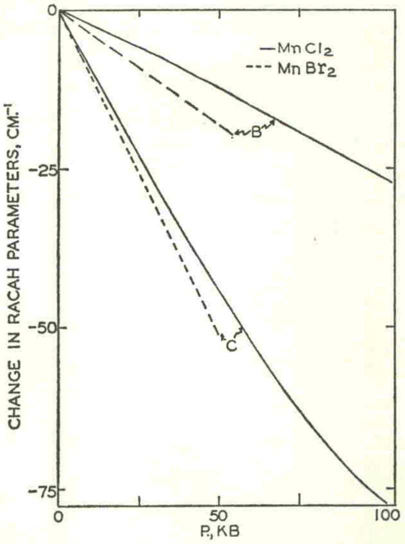

FIG. 19. Effect of pressure on the Racah parameters *B* and *C*—$MnCl_2$ and $MnBr_2$.

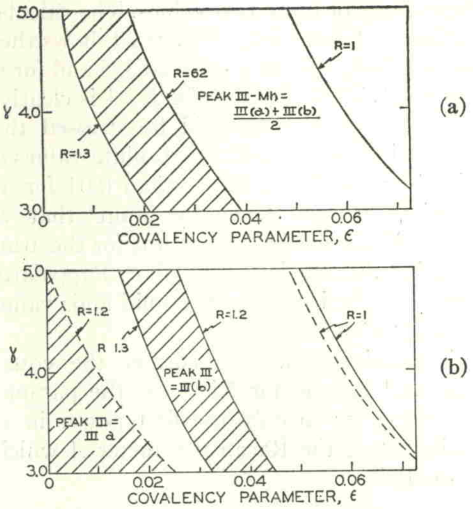

FIG. 20. (a) Allowed values of ϵ if peak III-Mn$=\frac{1}{2}$[IIIa)+IIIb)]. (b) Allowed values of ϵ if peak III-Mn=IIIa; if peak III-Mn=IIIb.

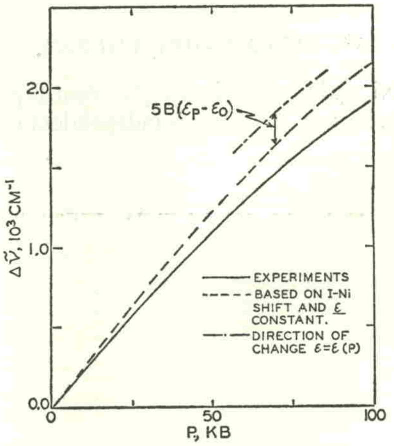

FIG. 21. The effect of the parameter ϵ in calculating shifts for peak II-Ni in $NiCl_2$.

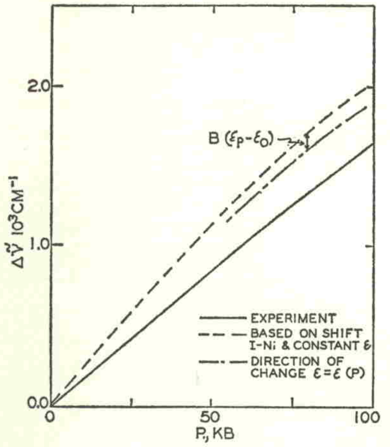

FIG. 22. The effect of the parameter ϵ in calculating shifts of peak III-Ni in $NiCl_2$.

or the average of these two values. The calculated R is a function of γ and ϵ only. Figure 20 shows the allowed values of ϵ for values of γ between 3–5 and for values of R between 1.2–1.3. The line for $R=1$ is clearly beyond experimental error. It should be stressed that these curves are independent of the absolute values of B and C. Clearly ϵ can be no larger than 0.04 for any fixed value of γ. It was shown by Stout[5] that values of $\epsilon=0.13$–0.15 are needed to account for the atmospheric peaks using the free ion value of B. Pappalardo[6] using a value of B obtained from the solid finds values of ϵ in the range 0.03–0.05.

It is relatively easy to correct the equations of Tanabe and Sugano for Ni^{++} for the parameter ϵ, if one keeps terms to only the first power in ϵ. The ϵ^2 terms introduce the Racah parameter A which cannot be evaluated

$$\text{I}-\text{Ni}=10Dq^*=10Dq+(A-8B)\epsilon \qquad (15)$$

$$\text{II}-\text{Ni}=15Dq^*+1.5B-3B\delta^*+5B\epsilon \qquad (16)$$

$$\text{III}-\text{Ni}=15Dq^*+13.5B+3B\delta^*-B\epsilon, \qquad (17)$$

where

$$\delta^*=[(10Dq^*-9B)/12B]^2\ll 1.$$

Peak I-Ni again determines Dq^*. From Eqs. (16) and (17), it can be seen that, if B is independent of pressure, the pressure shift (but not the absolute energy of the transition) should be independent of ϵ. Figures 21 and 22 show the experimental shifts for these peaks compared with shifts calculated from Dq^* and the free ion value of B. In both cases too large a shift is predicted. If ϵ increases with pressure the calculated shift of peak II-Ni is increased by an amount proportional to $5B(\epsilon_P-\epsilon_0)$, i.e., the discrepancy is increased. The shift of peak III-Ni is decreased by an amount proportional to $-B(\epsilon_P-\epsilon_0)$. While this is in the right direction, any change of ϵ large enough to correct peak III-Ni will give absurd results for peak II-Ni. Evidently, this form of correction is not satisfactory for Ni^{2+}. It is not possible to say at present whether including terms in ϵ^2 would improve this situation.

These results show the power of the high-pressure optical technique in the study of crystal-field phenomena, in the identification of the III-Co peak, in the understanding of the effect of interionic distance on the Racah parameter, and in understanding the covalency parameter ϵ.

ACKNOWLEDGMENTS

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