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THE PRESSURE VARIATION OF THE ELASTIC CONSTANTS OF CRYSTALS

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Measurement of the pressure-dependence of elastic constants of crystals yields information pertinent to the experimental equation of state of solids, to theories of cohesion of solids, and to certain aspects of anharmonicity of lattice vibrations in solids. This paper discusses some of the information which has been provided by such measurements carried out on copper, silver, gold, aluminium, sodium, lithium, germanium, silicon and rubidium iodide. Experimental aspects are presented, and a few suggestions are made for extending the direct measurements of anharmonicity of lattice vibrations.

Introduction

The compressibility and variation of compressibility of crystals with pressure has long been the subject of quantitative experimental investigation by Bridgman whose results have provided the basis of many theoretical investigations of cohesion, notable among these are the works of Wigner & Seitz,[1] Frohlich,[2] and Bardeen[3,4] on compression of the alkali metals. Implications about the thermal properties of solids have been based on Bridgman's dilatational data, especially by Slater[5] whose establishment of the relation between Grüneisen's gamma and the pressure-dependence of the compressibility is familiar. Swenson is making very careful and elegant measurements of the compression of solids over a wide range of temperatures down to almost liquid helium temperature to obtain experimentally, temperature-dependent equations of state.[6] One may reasonably ask then whether it is worth while investigating the pressure-dependence of the shear elastic constants of crystals as well as that of the bulk modulus. It is hoped that the following discussion will serve to introduce the experimental aspects of the subject and to justify its pursuit by a brief indication of the sort of information about crystal binding forces and about anharmonic thermal properties of solids which reveals itself in interpretation of the data.

review

At the present time, few measurements have been made in this field. The pressure-dependence of the shear stiffnesses of a few polycrystalline solids has been studied by Birch,[7] and by Hughes.[8,9] Lazarus[10] in a pioneering paper reports on studies on single crystals of potassium and sodium chloride, copper–zinc, copper and aluminium with the ultrasonic pulse echo method. Very careful measurements on pressure- and temperature-dependence of elastic constants of germanium have been made by McSkimmin,[11] and mention must be made of the interesting work done by Anderson[12] seeking values of thermodynamic functions by measurements of the pressure- and temperature-dependence of the elastic constants of fused silica. Some interesting Russian work has appeared on the pressure-dependence of the elastic constants of cerium through the phase transition pressure at about 7·6 kb.[13] The remainder of the investigations, including those of copper, silver, gold,[14] aluminium, magnesium,[15] silicon,[16] sodium[17] and lithium[18] have been done at Case Institute of Technology, and our group at Princeton is engaged at the moment in the study of rubidium iodide.[19]

This paper is divided into three parts; (1) a discussion of techniques of measurement; (2) the interpretation of the results in terms of the various contributions to the cohesive energy of crystals; and (3) the implications of the results regarding the anharmonic thermal properties of solids. Some limitations and extensions of the methods will be considered briefly.

(1) Experimental methods

Most of the results to be discussed in this paper were obtained by the ultrasonic pulse echo method of measuring elastic constants.[20,21] This non-resonant method is well suited to the problems associated with an ambient consisting of a fluid at high pressure, but is probably less accurate than the phase comparison method used by McSkimmin[22] and Anderson.[12] Only the ultrasonic pulse echo method is considered here: for a discussion of other methods of measuring elastic constants reference should be made to Huntington's review article.[23]

The apparatus required for these experiments consists of a pressure-generating and measuring system, and a thick-walled steel vessel of sufficient size to contain the sample crystal, with one

electric lead in for the pulsed radio-frequency (r.f.). The pressure-generating system used for most of the measurements has been a fairly conventional pump with intensifier,[24] but a new system incorporating only a direct pump has been used to 5kb with complete reliability, with occasional runs to 10kb. It uses a re-entrant seal[25] on the critical high-pressure piston closure. Seals at other closures have been effected using armoured O-rings.[25] A manganin wire coil with nominal resistance 300 ohms has been used as the pressure sensor,[26] a conventional Wheatstone bridge being used to measure the changes of its resistance. The freezing pressure of mercury at 0°, 7640 kg/cm.^{2} after Bridgman,[26] has been taken as the high-pressure fixed point. Electrical leads have been made with the conventional Bridgman pipestone cones[27] and with careful fitting have proven completely reliable. Di-2-ethylhexyl sebacate (Octoil-S* or Plexol 201†) has been used as pressure fluid except for work with the alkali metals, where the high chemical reactivity demanded use of an isobutane–mineral oil mixture. The sebacate has the advantages of excellent lubricity and a low pressure coefficient of viscosity (silicone fluids are poor on both these points). All the above equipment has functioned for long periods of time with a minimum of maintenance.

Fig. 1 is a block diagram of the electronic components of a typical (and commercially available) ultrasonic pulse echo setup for measuring elastic constants of single crystals. The measurement to be made is basically one of time of travel of a pulse of 10 mc acoustic waves down the sample and back. The time mark generator is the heart of the apparatus, producing a set of markers to which the time measurements are referred. Stable markers are controlled by an oscillating quartz crystal maintained at constant temperature by an oven to assure its frequency stability. In operation, the time mark generator triggers simultaneously the pulse generator which emits about a 1 μsec. burst of 10 mc oscillations, and the sweep of high speed oscilloscope. The pulse of r.f. excites a 10 mc resonant X- or Y-cut quartz transducer cemented to the specimen crystal, generating an acoustic pulse of appropriate polarisation which echoes back and forth in the crystal. A variable sweep delay network on the oscilloscope calibrated against the time mark generator, enables precise measurements of the pulse transit time and especially of the *change* of transit time with pressure or any other independent variable. An invaluable improvement in technique for measuring changes of transit time was introduced by Eros & Reitz[28] who altered the electronics to permit display of the unrectified pulse whereas previously only the pulse envelope could be displayed. This removed the problem caused by changes of pulse shape with pressure.

The equation of motion describing the passage of an elastic wave through the crystal yields equations of the form $C = \rho v^2$, where ρ is the density of the crystal, v the velocity of the wave under consideration and C is the stress–strain ratio for the specific distortion caused by passage of that wave.[29] (The derivation, made treating the crystal as an elastic continuum is of course valid only if the wavelength is very much larger than the inter-ionic spacing, a condition rigorously met by the 10-mc disturbances applied in the measurements.) For a cubic crystal cut with [110]

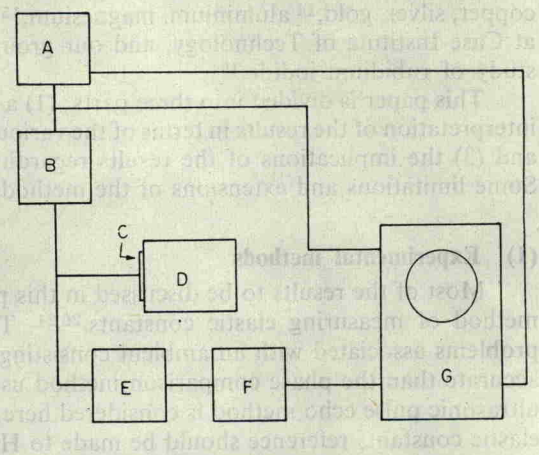

Fig. 1. *Block diagram of ultrasonic pulse echo components*

A Time mark generator (Tektronix TM 181 with crystal oven) B Pulse generator (Arenberg PG–650C) C quartz crystal transducer D single crystal sample E pre-amplifier (Arenberg PA–620–SN) F wide band amplifier (Arenberg WA–600–B) G oscilloscope (Tektronix Model 585 with Type CA dual traced plug-in unit. The Oscilloscope sweep delay helipot has been replaced by a more sensitive voltage divider)

* Octoil–S is a vacuum diffusion pump fluid sold by Consolidated Electrodynamics Corp., Rochester, New York.
† Plexol 201 is available from Rohm & Haas Chemical Co., Resinous Products Division, Philadelphia 5, Pa, U.S.A.