state and so is not expected to be excited directly with an intensity comparable with the $M1$ transitions exciting the 0+, 1+, or 2+ levels. It is therefore doubtful that the line observed by Adyasevich excites the state of 1860 (4+, 3+). The intensity of the high-energy $M1$ transitions is at most 0.6% gammas per neutron captured whereas the weakest low-energy line that can be detected with the present equipment is >1%. Thus excitation in addition to a direct transition from the capturing state is required and it is possible that the low-energy data might miss the de-excitation of a weakly populated state and this is indeed suggested by the unaccounted for x-rays observed.

The gamma rays of 1403 and 1498 kev have an energy difference of 95±7 kev and fit energetically into the decay scheme assumed to come from a state at 2710±6 kev with spin 1 and even parity. Such a state should be excited directly by means of an $M1$ transition from the capturing state but no such high-energy transition is observed by either Kinsey and Bartholomew[30] or by Adyasevich *et al.*[5] It is, therefore, uncertain that these lines actually originate from a 1+ state at 2710 kev.

It is not possible to assign the higher energy lines observed in this work with sufficient reliability merely on an energy balance argument. Greater precision and resolution or coincidence experiments are necessary to complete the decay scheme above 2-Mev excitation. Measurements on $\mathrm{Cd}^{113}(d,p)\mathrm{Cd}^{114}$ would be of great value in verifying and extending the decay scheme. Muehlhause[1] has observed that an average of 4.1 cascade gamma rays are emitted in the $\mathrm{Cd}^{113}(n,\gamma)\mathrm{Cd}^{114}$ reaction and it must be expected that the coincidence spectrum will be very complex.

ACKNOWLEDGMENTS

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Dependence of the Pure Quadrupole Resonance Frequency on Pressure and Temperature*

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Measurements of the pure quadrupole resonance frequency (ν) of the Cu^{63} nucleus in cuprous oxide, and the Cl^{35} nucleus in potassium chlorate and paradichlorobenzene have been made as a function of pressure in the range 1 to 10 000 kg/cm² for temperatures between −77°C and 100°C. A theory is presented in which the static value of the electric field gradient tensor (ϕ_{ij}^0) and the amplitudes ξ_i^0 of the normal modes of the lattice vibrations play a central role. The volume dependence of these quantities can be deduced from ν-*versus*-volume isotherms which are constructed from the experimental data by using the equation of state. Information on the latter is augmented by theory. It is found that the temperature variation of the resonance frequency at atmospheric pressure can be understood by considering not only the explicit temperature dependence of the vibration amplitudes, but also by including the appreciable effects of the volume expansion on q_0 and ξ_i^0. Furthermore, the pressure dependence is found to be explicable in terms of the volume dependence of q_0 and ξ_i^0. In $\mathrm{Cu_2O}$, it is found that q_0 depends on volume roughly as V^{-1}, thereby indicating an ionic character for this crystal. On the other hand, in paradichlorobenzene, $q_0 \propto V^n$, with $0<n<0.04$, thus exhibiting the effect of an increase in the intermolecular hybridization of the C−Cl covalent bond.

I. INTRODUCTION

Since its discovery,[1] the pure quadrupole splitting of the nuclear spin energy levels in solids has been investigated as a function of temperature. Bayer[2] proposed a theory, later generalized by Kushida[3] and Wang,[4] which explained the salient features of this effect. It failed, however, to give detailed agreement with experiment.[5] According to this theory, the average internal field gradient at the nucleus decreases with increasing temperature solely because of the increase in the amplitude of the thermal vibrations.

It seems fairly obvious that a strain deformation at constant temperature will also alter the electric field gradients in the solid lattice. Uniaxial compression in cubic crystals was first attempted by Watkins and

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Pound.[6] They found that the application of uniaxial stress to alkali halide crystals broadened the magnetic resonance lines in an irreversible manner. Presumably, the deformation was not homogeneous and plastic flow occurred, creating a nonreversible distribution of quadrupole splittings throughout the crystal. Recently, Shulman[7] has succeeded in obtaining a reversible and rather homogeneous deformation by uniaxial compression of an indium antimonide crystal. By using high hydrostatic pressures, large homogeneous deformations can be expected. If the symmetry around the nuclei is cubic, the field gradient will remain zero, but the quadrupole interaction in noncubic crystals will be changed by hydrostatic pressure.

Several workers[8–11] have independently found such a dependence of the quadrupole splitting upon the application of hydrostatic pressure. The splitting depends in general on the amplitude ξ_i^0 of the normal modes of vibration and on the electrostatic lattice potential at the nucleus V_e through the principal value of the field gradient q_0 and the asymmetry parameter defined by

$$q_0=\frac{\partial^2 V_e}{\partial z^2} \quad \text{and} \quad \eta_0=\left(\frac{\partial^2 V_e}{\partial x^2}-\frac{\partial^2 V_e}{\partial y^2}\right)\Big/\frac{\partial^2 V_e}{\partial z^2},$$
$$0<|\eta_0|<1.$$

The pure quadrupole resonance frequencies can be expected to be a function of volume through q_0, η_0 and ξ_i^0. Phenomenologically, one can express the temperature and pressure dependence of the pure quadrupole splittings by the thermodynamical relations:

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial P}\right)_T=\frac{V}{\nu}\left\{\frac{\partial\nu}{\partial q_0}\frac{dq_0}{dV}+\frac{\partial\nu}{\partial\eta_0}\frac{d\eta_0}{dV}+\sum_i\frac{\partial\nu}{\partial\xi_i^0}\left(\frac{\partial\xi_i^0}{\partial V}\right)_T\right\}\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{1}$$

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial T}\right)_P=\frac{V}{\nu}\left\{\frac{\partial\nu}{\partial q_0}\frac{dq_0}{dV}+\frac{\partial\nu}{\partial\eta_0}\frac{d\eta_0}{dV}+\sum_i\frac{\partial\nu}{\partial\xi_i^0}\left(\frac{\partial\xi_i^0}{\partial V}\right)_T\right\}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P+\frac{1}{\nu}\sum_i\frac{\partial\nu}{\partial\xi_i^0}\left(\frac{\partial\xi_i^0}{\partial T}\right)_V. \tag{2}$$

The last term in Eq. (2) represents the effect considered by Bayer. However, the effect of the volume expansion represented by the bracket term is by no means negligible, and an adequate analysis of the observed temperature variation of ν requires a knowledge of the volume variation as well.

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial V}\right)_T=\frac{1}{\nu}\left\{\frac{\partial\nu}{\partial q_0}\frac{dq_0}{dV}+\frac{\partial\nu}{\partial\eta_0}\frac{d\eta_0}{dV}+\sum_i\frac{\partial\nu}{\partial\xi_i^0}\left(\frac{\partial\xi_i^0}{\partial V}\right)_T\right\}, \tag{3}$$

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial T}\right)_V=\frac{1}{\nu}\sum_i\frac{\partial\nu}{\partial\xi_i^0}\left(\frac{\partial\xi_i^0}{\partial T}\right)_V. \tag{4}$$

Equation (4) represents Bayer's effect, the temperature dependence of ν at constant volume. The volume dependence of ν represented in Eq. (3) consists of a temperature-independent part (first two terms) and a temperature-dependent part (third term). Thus a complete analysis of both the volume and temperature dependence of ν requires a knowledge of ν over a wide range of temperature and volume. Conversely, one can expect to obtain from such an analysis the volume dependence of the internal field gradients and the volume dependence of the vibration amplitudes. This analysis is carried out in the present paper for three substances which are thought to give representative illustrations of the results to be expected.

Consider, for example, an ideal ionic lattice. Assume further that all interionic distances vary as $V^{\frac{1}{3}}$. In such a crystal q_0 will be inversely proportional to V, and η_0 will be constant. On the other hand, consider a molecular crystal. Here, the gradient is predominantly a property of the covalent bond[12] in the molecule and in the zeroth approximation is independent of volume. However, it is well known that the quadrupole splitting in a molecular lattice is not exactly the same as in the free molecule and may be about 10% less. Compression of the molecular crystal can be expected to increase the hybridization of the intramolecular bond by bonding to neighboring molecules. This will cause a decrease of q_0 with decreasing volume. Most solids, of course, will show a behavior lying somewhere between these extremes.

II. EXPERIMENTAL METHOD

A brief description of the experimental method is as follows: The sample, in the form of a dense, powdered suspension in a pressure transmitting liquid, is placed within and around a radio-frequency coil which serves as the tuning inductance of a Pound-Knight-Watkins[13,14] spectrometer. A hydraulic press compresses the transmitting fluid, thereby producing an increase in the hydrostatic pressure to which the sample crystallites are subjected. The change in the resonance frequency of the sample which results is then measured. Thus, the experimental arrangements include (*a*) the bomb and plug assembly consisting of the coil and sample holder, a beryllium copper pressure-containing cylinder, and a BeCu high-pressure coaxial electric plug; (*b*) the high-

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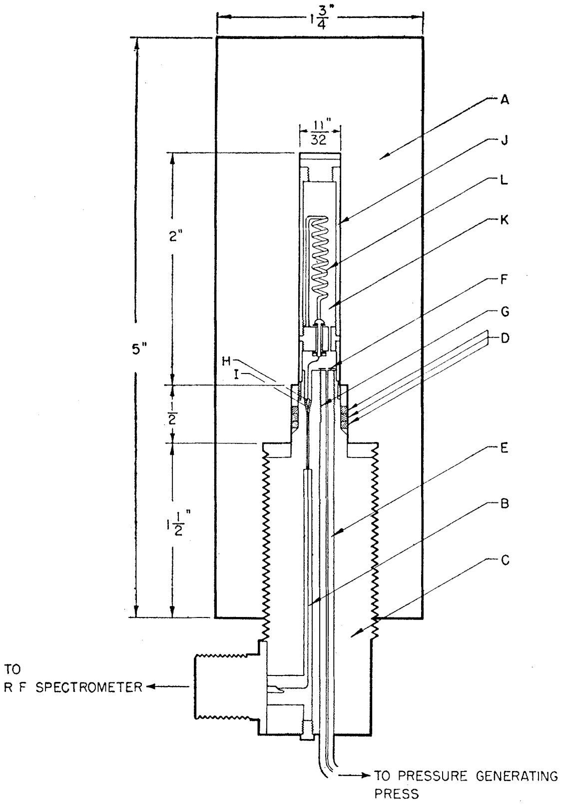

Fig. 1. High-pressure bomb and electrical plug assembly. (*A*) Beryllium copper bomb. (*C*) Beryllium copper electrical plug. (*D*) Sealing washers. (*H*) Conical seal for electrical terminal. (*L*) Radio-frequency coil. (*E*) Stainless steel connecting tubing.

pressure ram and pressure-measuring equipment; and (*c*) the electronic equipment consisting of the Pound-Knight-Watkins spectrometer, a phase-sensitive detector and a lock-in amplifier.

Figure 1 is a diagram of the bomb and plug assembly. The high-pressure bomb (*A*) is constructed of beryllium copper, whose special properties in this application have already been described.[15] The nonmagnetic property of BeCu is not essential in this zero field experiment. The small size and great strength of this bomb enable it to be temperature-controlled by constant temperature baths in spaces as small as 2 in. in width, while it is subjected regularly to internal pressures up to 10 000 kg/cm^2. Both the radio-frequency electrical lead (*B*) and the pressure-transmitting liquid are led into the bomb through the BeCu electrical plug (*C*), which is sealed against leak past the threads by the sealing washers (*D*) of lead and copper, which operate on Bridgman's unsupported area principle. Hardened stainless steel tubing (*E*) $\frac{1}{8}$ in. o.d. and 0.025 in. i.d., which is quite flexible when coiled, provides for convenient transmission of the pressure from the pressure-generating cylinder to the bomb.[16] The tubing is threaded and soft-soldered into the plug (*C*). A small copper sheet (*F*) with a tiny pinhole for admission of liquid soldered over the end of the tubing is very effective in preventing leak past the threads (*G*). The electrical lead is insulated at the coned sealing stem (*H*) by a conical pipestone washer (*I*), and is connected to the radio-frequency coil (*L*). The sample holder (*J*) contains the powdered specimen (*K*) suspended in the pressure transmitting medium. Petroleum ether was used as a pressure transmitting medium for temperatures around 0°C, while kerosene was used around 100°C. At -77°C it was found that a 50–50 mixture of *n*-pentane and 2-methyl-butane is capable of going to 10 000 kg/cm^2 without any indication that the hydrostatic nature of the compression is lost. The pure quadrupole resonance itself, sensitive as it is to nonhydrostatic strain,[6] serves as a very good check on the degree of homogeneity of the applied compression.[17] Since the width of the lines did not change by more than 10% even at the highest pressure, it may be concluded that the pressure is hydrostatic to at least one part in a thousand. Dissolution of the organic specimens in the transmitting fluids was avoided by the simple trick of first saturating the liquid with the material to be suspended, then adding the saturated solution to the powdered specimen. Temperature regulation was achieved by immersing the bomb in a constant temperature bath. A water bath whose temperature was constant to within ± 0.05°C was used above room temperature. Below room temperature, ice and water or dry ice and petroleum ether mixtures gave a temperature stability of about ± 0.05°C and ± 0.2°C, respectively.

The pressure-generating section was the standard Bridgman press.[18] The pressure was measured with an accuracy of about 3 kg/cm^2 at each pressure by observing the change of resistance of a coil of manganin wire with a Carey-Foster bridge.[18]

The electronic detection equipment was the customary Pound-Watkins spectrometer with a lock-in amplifier and a phase-sentitive detector[6] with 30 cps on-off Zeeman modulation and recorder display. The effects of pickup from the on-off modulating field were diminished considerably by means of a high-pass RC filter in the grid circuit of the 6J6 oscillator. The cutoff frequency of this filter was roughly 500 cps. The resonance frequency was determined by beating the spectrometer frequency against that of a crystal-calibrated L.M. heterodyne frequency meter (type CKB-74028). Using this technique, the resonance frequency could be measured to better than 1 kc.

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III. EXPERIMENTAL RESULTS

Measurements of the pure quadrupole resonance frequency as a function of pressure in the range 1 to 10 000 kg/cm^2 for three different temperatures ranging from -77°C to $+100$°C have been made for the Cl^{35} nucleus in KClO$_3$, the Cu^{63} nucleus in Cu$_2$O, and the Cl^{35} nucleus in paradichlorobenzene.

a. Potassium Chlorate, KClO$_3$

The sample was Mallinkrodt analytical reagent grade material in the form of granules. It consists of a minimum of 99% KClO$_3$ with sodium and BrO$_3$ the principal impurities in the lattice. In Fig. 2 is shown the pressure dependence of the resonance frequency at -77°C, 24.6°C, and 84.7°C. In addition to these data, recent experiments by Livingston[19] show that $(\partial\nu/\partial P)_{P=0}$

$=6.5$ cps/(kg/cm^2) and $\nu_{P=0}=28.9534$ Mc/sec at 196°C.

At room temperature the intensity of the line was constant during the increase in pressure until 6000 kg/cm^2, at which point the intensity began to fall with increasing pressure while the line width remained constant, until at 10 000 kg/cm^2 the intensity was one third of its atmospheric pressure value. Similar results were observed during the 84.7°C run, except that the onset of the decrease in intensity began about 1000 atmos higher in this case. For both runs the intensity remained at its 10 000 kg/cm^2 value during the decrease of pressure. The loss of intensity may be connected with the polymorphic transition previously observed by Bridgman.[20] He found a sluggish transition at 6000 kg/cm^2 for $T=25$°C and 6700 kg/cm^2 for $T=85$°C. The sluggishness of the transition probably accounts for our ability to follow the low-pressure phase as high as 10 000 kg/cm^2 with no attendant increase of the intensity during the relatively rapid decrease of pressure.

b. Cuprous Oxide, Cu$_2$O

This sample was Bakers reagent grade powdered material consisting of 97.4% Cu$_2$O the principal impurity being Cu$_2$Cl. The line width in Cu$_2$O was substantially constant throughout the pressure range. However, the signal intensity decreased at all temperatures with increasing pressure until at 10 000 kg/cm^2 the intensity was reduced to one half of its initial value. The pressure dependence of the resonant frequency at -77°C, 25°C, and 98.5°C is shown in Fig. 3. It will be observed that at all temperatures the resonance frequency, within the experimental error, is a linear function of the pressure.

c. Paradichlorobenzene, p-C$_6$H$_4$Cl$_2$

This sample was Eastman Kodak white-label grade granular material. The observation of the quadrupole resonance in paradichlorobenzene is complicated by the existence of three polymorphic phases. Dean[21] measured the temperature dependence of two of these phases, measured the temperature dependence of two of these phases, namely, the low-temperature α phase and the high-temperature β phase. He found that the resonant frequency of the α phase is higher than that of the β phase by approximately 25 kc/sec. In addition, he produced for a short time a third "anomalous" phase by accidentally subjecting the single crystal sample to a strong compressive stress by thermal expansion inside

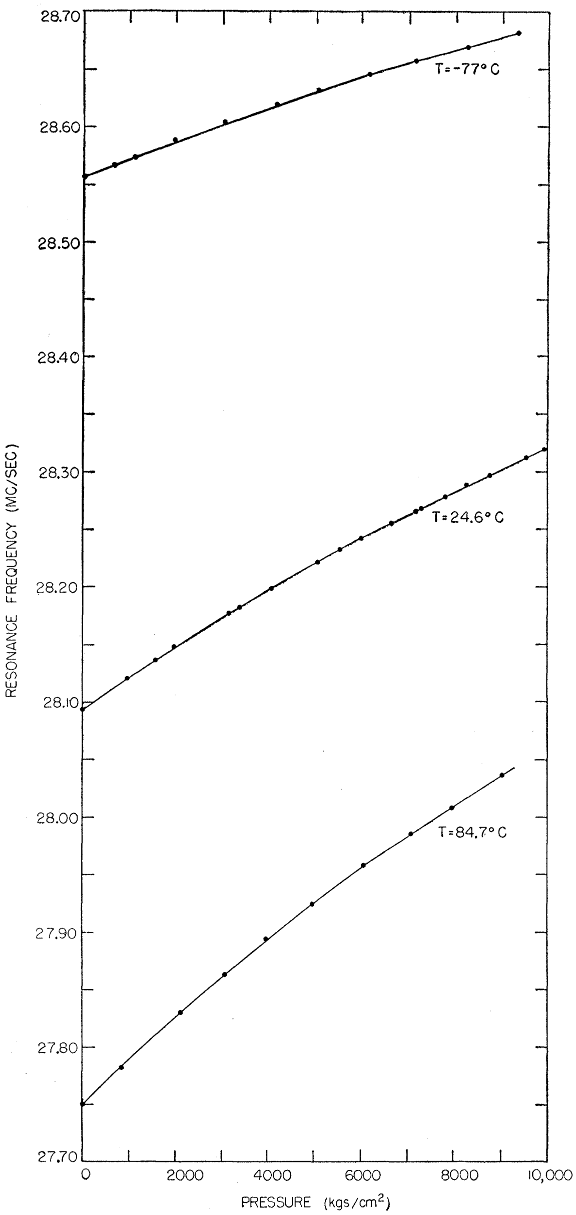

FIG. 2. The pure quadrupole resonance frequency of the Cl^{35} nucleus in KClO$_3$ as a function of pressure for three temperatures.

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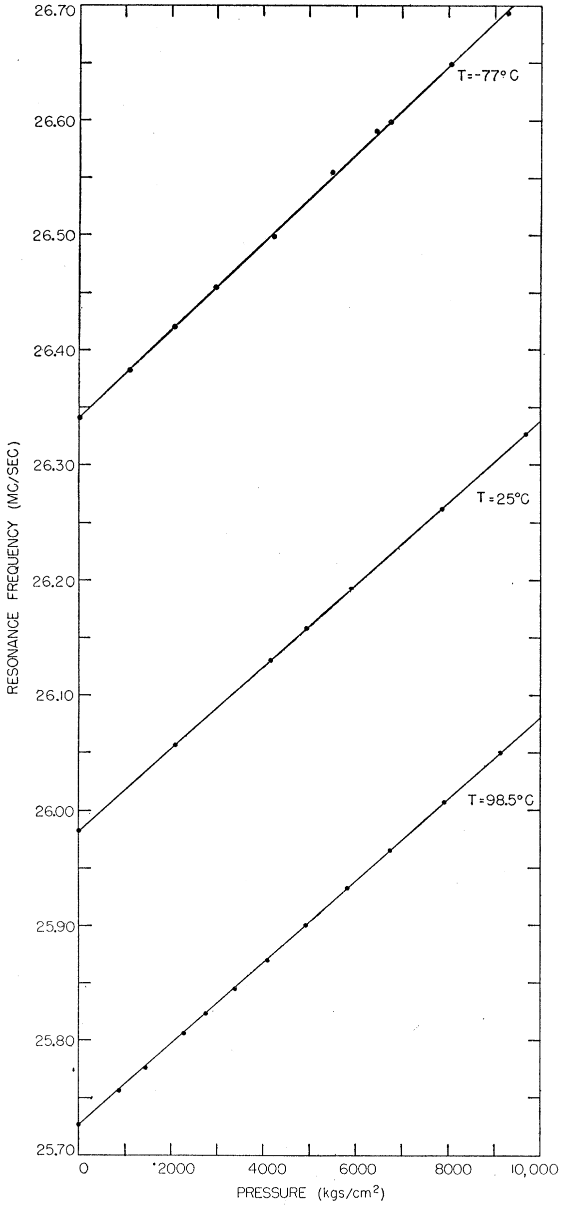

FIG. 3. The pure quadrupole resonance frequency of the Cu^{63} nucleus in Cu_2O as a function of pressure for three temperatures.

a metal container of fixed volume. He found that the anomalous phase was about 460 kc/sec higher than the α or β phase but was unable to maintain the crystal in the new phase long enough to make detailed studies of its temperature variation.

We observed all three phases of p-$C_6H_4Cl_2$ during the $T=24.8$°C run shown in Fig. 4. At atmospheric pressure the α-phase is observed,[21] its frequency increasing with increasing pressure until, at 1600 kg/cm^2, the line quickly disappears. The line appears again 436 kc/sec higher, with an intensity and line width which is about the same as that for the α phase. This new high-pressure phase may be identified as Dean's "anomalous" γ phase. Above 1600 kg/cm^2 the γ-phase line was quite stable. On reaching 2200 kg/cm^2, $\partial\nu/\partial P$ begins to decrease markedly until, at 8500 kg/cm^2, $\partial\nu/\partial P=0$. Above this pressure there is the suggestion that $\partial\nu/\partial P$ may become negative. On decreasing the pressure the γ phase can be followed back even below 1600 kg/cm^2, until, at about 750 kg/cm^2, it disappears only to reappear again about 27 kc/sec below the α phase. This new phase can be identified as Dean's β phase. The line width was about 50% broader and the peak intensity less than that of the α or γ phase. The total integrated intensity of the β-phase line is roughly equal to that of the α or γ line. The β phase is metastable at room temperature and returns to the α phase in a time which is very sensitive to the pressure. For instance, at amospheric pressure this phase lasts for a time of the order of minutes, while at 600 atmos it can be observed for the order of one day. Because of the long relaxation time of this metastable state it is possible to increase and decrease the pressure on the the β-phase line to determine its extent. It was found that the transition to the γ phase occurred at about 1600 atmos. The quickness of the relaxation to the α-phase at the lower pressure limited the observation in this range to 300 kg/cm^2.

At 0°C the atmospheric pressure phase is again the α phase. As we see in Fig. 5, this phase disappears at 400 kg/cm^2, reappearing 435 kc higher in the γ phase. On increasing the pressure, $\partial\nu/\partial P$ becomes zero at about 7800 kg/cm^2 and the indications that it goes negative above this pressure become more marked. On decreasing the pressure there is again a reproducibility of the increasing pressure points except that the γ phase continues to persist right down to atmospheric pressure.

If one observed the resonance in perfectly dry paradichlorobenzene, the α phase is found at -77°C. Upon addition of the transmitting fluid (petroleum ether or a 50–50 mixture of n-pentane and 2-methyl-butane)

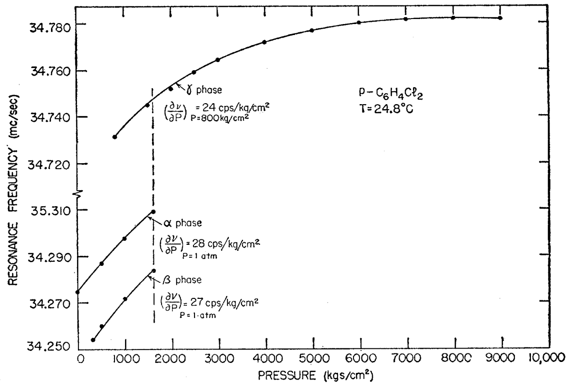

FIG. 4. The pure quadrupole resonance frequency of the Cl^{35} nucleus in paradichlorobenzene as a function of pressure at $T=24.8$°C. The α, β, and γ phases are polymorphic modifications which are produced by hydrostatic pressure at room temperature.

the α phase disappears even at atmospheric pressure, and in its place the γ phase appears. The appearance of the γ phase upon the addition of paraxylene or benzene has been observed independently by Dean and Lindstrand.[9] As may be seen in Fig. 6, an increase of the pressure on the γ phase results in a slight increase in the frequency up to about 1000 kg/cm². Beyond this pressure the resonance frequency drops quite markedly with the pressure. In Table I the frequency of the γ phase at $P=1$ kg/cm² is listed as a function of temperature. An attempt to study sodium chlorate over an extended pressure range failed, because it combined explosively at about 2000 atmos with the transmitting medium.

IV. THEORY

Pure quadrupole resonance absorption occurs at frequencies which correspond to transitions between the energy levels of the Hamiltonian[1] describing the interaction of the electric field gradient tensor (ϕ_{ij}) and the nuclear quadrupole moment,

$$\mathcal{H}=\frac{eQ}{2I(2I-1)}\{\phi_{xx}I_x^2+\phi_{yy}I_y^2+\phi_{zz}I_z^2+\phi_{xy}(I_xI_y+I_yI_x)+\phi_{xz}(I_xI_z+I_zI_x)+\phi_{yz}(I_yI_z+I_zI_y)\},\quad (5)$$

where e is the electronic charge, $\mathbf{I}$ is the nuclear spin operator, and Q is the nuclear quadrupole moment. Lattice vibrations cause the components $\phi_{ij}=\partial^2V_e/\partial x_i\partial x_j$ of the field gradient tensor to fluctuate with time at a frequency which is much higher than that corresponding to the energy level separation ($\sim10^6$–10^8 cps). Thus only the time average of ϕ_{ij} enters into the expression for the energy levels of the system. Consider specifically a (ϕ_{ij}) tensor which is axially symmetric in the static case, and assume that the lattice vibrations cause: (a) a time variation in the magnitude of the principal axis $q=\phi_{zz}$ of the quadrupole tensor about some equilibrium value; (b) a time variation in the angular orientation of the ϕ_{ij} tensor relative to its static or equilibrium orientation; (c) a small time variation of the asymmetry parameter around its static value, which is assumed zero. The asymmetry parameter η_0 is not zero in the investigated crystals $KClO_3$ and paradichlorobenzene,[22] but it is very small and will be neglected. The following analysis can be readily extended to include the effect of η. In that case, separate experimental data on η as a function of temperature and volume are also required. From a zero field experiment with $I=\frac{3}{2}$, this information is not available. It follows from Eq. (5) that the frequencies of transitions induced by the radio-frequency magnetic field can be written as[2,3]

$$\nu(I,m_z\leftarrow m_{z-1})=C(I,m_z\leftarrow m_{z-1})\langle q(t)\rangle_{\mathrm{Av}}(1-\tfrac{3}{2}\langle\theta^2(t)\rangle_{\mathrm{Av}}),\quad (6)$$

where $\langle q(t)\rangle_{\mathrm{Av}}$ is the time average value of the magnitude of the maximum principal axis of the electric field gradient tensor, $\langle\theta^2(t)\rangle_{\mathrm{Av}}$ is the time average value of the square of the angle of inclination of the maximum principal axis of ϕ_{ij} relative to its equilibrium direction, $C(I,m_z\leftarrow m_{z-1})$ is a constant which depends only on I, Q, m_z, and the final state. For integral spin I there are I transition frequencies, and for half-integral spin I there are $I-\frac{1}{2}$ transitions; hence, $C(I,\Delta m_z)$ takes on I or $I-\frac{1}{2}$ values, depending on the magnitude of the nuclear spin.

TABLE I. Frequency of the γ phase of p-$C_6H_4Cl_2$ *versus* temperature at $P=0$.

Frequency Mc/sec	Temperature °C
34.710[a]	24.8
34.785	0
34.988	−77

[a] Extrapolated to $P=0$.

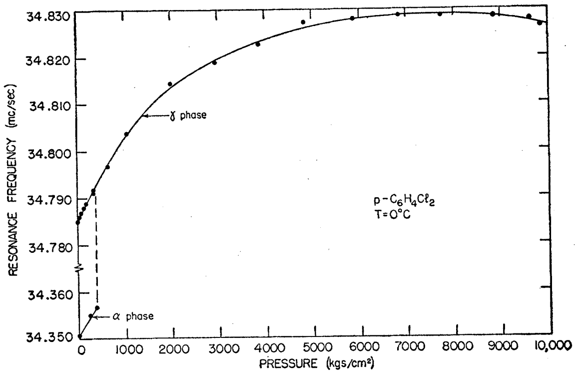

FIG. 5. The pure quadrupole resonance frequency of the Cl^{35} nucleus in paradichlorobenzene as a function of pressure at $T=0°C$.

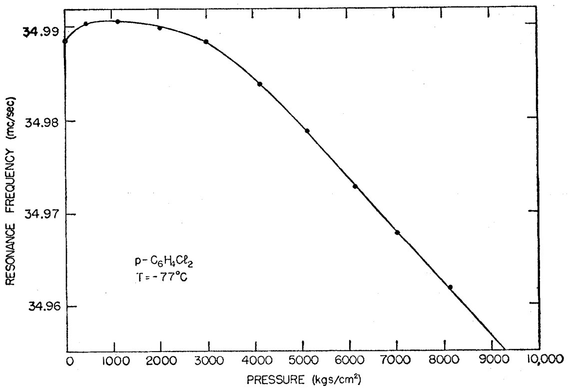

FIG. 6. The pure quadrupole resonance frequency of the Cl^{35} nucleus in the γ phase of paradichlorobenzene as a function of pressure at −77°C.

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[22] C. Dean, Phys. Rev. **86**, 607 (1952).

The temperature variation of the resonance frequency results from the temperature variation of $\langle\theta^2\rangle_{\text{Av}}$ and $\langle q(t)\rangle_{\text{Av}}$.

The quantitative relation between $\langle\theta^2(t)\rangle_{\text{Av}}$, $\langle q(t)\rangle_{\text{Av}}$ and temperature can be found by expanding $\theta^2(t)$ and $q(t)$ in terms of the normal modes of vibration of the lattice.[3] If $\xi_i^0 \cos\omega_i t$ is the ith normal coordinate, then the resonant frequency of a particular spin transition can be written as

$$\nu=\nu_0\left[1-\tfrac{3}{4}\textstyle\sum_i (\xi_i^0)^2 A_i\right]. \tag{7}$$

Here A_i is defined by $A_i=\alpha_i-\frac{2}{3}\delta_{ii}$, where α_i and δ_{ii} are coefficients in the following expansion:

$$\theta=\textstyle\sum_i \alpha_i\xi_i+\cdots, \tag{8}$$

$$q=q_0(1+\textstyle\sum_i \beta_i\xi_i+\sum_{ij}\delta_{ij}\xi_i\xi_j+\cdots). \tag{9}$$

Higher-order terms in the expansion are neglected. This is consistent with the approximation $\langle\theta^2\rangle_{\text{Av}}\ll 1$ used to derive Eq. (6). The temperature dependence appears by recognizing that the amplitude of vibration of the ith mode is determined by setting the energy of that mode equal to the mean energy of a corresponding harmonic oscillator, i.e.,

$$\frac{1}{2}\omega_i^2(\xi_i^0)^2=\hbar\omega_i\left(\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right). \tag{10}$$

It follows that the relation between ν and the temperature is

$$\nu=\nu_0\left[1-\frac{3}{2}\sum_{i=1}^{N}\frac{A_i}{\omega_i^2}\hbar\omega_i\left(\frac{1}{2}+\frac{1}{\exp(\hbar\omega_i/kT)-1}\right)\right], \tag{11}$$

where ω_i is the eigenfrequency of the ith mode of vibration and

$$\nu_0=\frac{eQq_0\frac{3}{2}(2m_z-1)}{2I(2I-1)}; \tag{12}$$

q_0 is the value of the field gradient in the rigid lattice, excluding even zero-point vibrations. The preceding formulation includes both the effect of the Debye waves and of the intramolecular vibrations that constitute "optical modes" which are often regarded as discrete eigenfrequencies. For the Debye waves, the summation term in (11) becomes

$$-\frac{3}{2}\left(\frac{\bar{A}}{\langle m_a c^2\rangle_{\text{Av}}}\right)9kT\left(\frac{T}{T_D}\right)^3\int_0^{(T_D/T)}\left(\frac{1}{2}+\frac{1}{e^x-1}\right)x^3dx. \tag{13}$$

In this case $\bar{A}$ is a constant of the order of 1, m_a and c are, respectively, an effective atomic mass and an effective propagation velocity.

Unless experiments are carried out at extremely low temperatures, it is useful to split the lattice vibrations into low- and high-frequency terms, depending upon whether they are larger or smaller than $\omega_M=kT_M/\hbar$, where T_M is the lowest temperature used in the experiments. For temperatures above the Debye temperature, the acoustical Debye modes may always be included with the low-frequency terms. The temperature variation of the low-frequency terms can be expressed simply by making use of an expansion valid in the range $x=\hbar\omega/(kT)\leq 1$, *viz.*,

$$\left(\frac{1}{2}+\frac{1}{e^x-1}\right)=\frac{1}{x}+\frac{x}{12}+O(x^3). \tag{14}$$

Equation (14) is very accurate; the first two terms give a result only 1.5% too large in the very unfavorable case, $x=2$. Thus, one can write Eq. (11) as

$$\nu=\nu_0\left\{1-\frac{3}{2}kT\sum_1^M\frac{A_i}{\omega_i^2}-\frac{\hbar^2}{8kT}\sum_1^M A_i+\Omega(T)\right\}, \tag{15}$$

where

$$\Omega(T)=-\frac{3}{2}\sum_{i=M+1}^{N}\frac{A_i}{\omega_i^2}\hbar\omega_i\left(\frac{1}{2}+\frac{1}{e^x-1}\right). \tag{16}$$

$\Omega(T)$ represents the contribution of the high-frequency vibrations to ν. Owing to the appearance of the $1/\omega_i$ factor in the terms of the sum, the high-frequency terms contribute generally much less than the low-frequency terms, and can often be neglected in practice. If we assume this to be the case and set $\Omega(T)=0$, we can write Eq. (15) in the form:

$$\nu=(a+b'T+c'/T)=a(1+bT+c/T), \tag{17}$$

where

$$a=\nu_0=\frac{eQq_0}{2I(2I-1)}(3m_z-\tfrac{3}{2}), \tag{18}$$

$$b=\frac{b'}{a}=-\frac{3}{2}k\sum_1^M\frac{A_i}{\omega_i^2}=-\frac{3k}{2}M\left\langle\frac{A}{\omega^2}\right\rangle, \tag{19}$$

$$c=\frac{c'}{a}=-\frac{\hbar^2}{8k}\sum_1^M A_i=-\frac{\hbar^2}{8k}M\langle A\rangle. \tag{20}$$

Equations (17)–(20) are central in the analysis of the temperature and pressure variation of the resonance frequency.

The quantity a defined in Eq. (18) is directly proportional to q_0, the equilibrium or static value of the principal axis of the field gradient tensor. The quantity b cannot be interpreted simply in the general case of molecular vibration or Debye lattice vibrations, because A_i has no simple description in the general case. For certain modes of vibration, however, A_i has a simple physical significance. For example, if one neglects the effect of the molecular stretching motion on the average value of q_0[23]; and if one further considers a simple normal mode of vibration which corresponds to a

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[23] This is generally valid since the displacements of the stretching motion are very small relative to the displacements of the rotatory motions in the low-frequency region.

bending motion of the direction of the principal axis q around an axis perpendicular to the direction of q, then it can be shown[2,3] that A_i^{-1} is the moment of inertia of this bending mode of vibration. In the general case, one can say only that A_i^{-1} has the dimension and order of magnitude of the moment of inertia of a molecular vibration. Writing $A_i=(\Theta_i)^{-1}$, where Θ_i is to be considered as an "equivalent moment of inertia," one can see from Eq. (19) that b is proportional to the average value of $(\Theta_i\omega_i^2)^{-1}$, where the average is carried out over the modes $0<\omega<\omega_M$. From Eq. (20) it is seen that c represents the average of Θ_i^{-1}, again over the low-frequency modes.

It must be emphasized that measurements of ν as a function of temperature *at constant pressure* do not suffice to determine the quantities a, b, and c. These parameters are functions of the volume, and in the thermal expansion accompanying constant pressure measurements, a, b, and c can be expected to change. The temperature variation predicted by Eq. (17) can be checked, and the magnitudes of a, b, and c can be found only from measurements of ν as a function of temperature *at constant volume.* Thus, it can be seen that an adequate analysis of the dependence of the pure quadrupole resonance frequency on the thermodynamic state of the solid can be achieved only when the resonance frequency is known as a function of volume for a series of different temperatures. If such information is available, then one cannot only check the form of the temperature dependence predicted by Eq. (17), but also determine the magnitude of a, b, and c and their dependence on volume. The magnitudes of a, b, and c at a given volume determine q_0, $\langle 1/\Theta\omega^2\rangle$, and $\langle 1/\Theta\rangle$, as is seen from Eqs. (18), (19), and (20). The information regarding the volume dependence of q_0, ω_i, and A_i can be represented in the following way:

$$\begin{aligned} q_0(V)&=q_0(V_0)(V/V_0)^{n(V)}, && \text{(A)} \\ \omega_i(V)&=\omega_i(V_0)(V/V_0)^{-\gamma_i}, && \text{(B)} \quad (21) \\ A_i(V)&=A_i(V_0)(V/V_0)^{+\sigma_i}, && \text{(C)} \end{aligned}$$

where V/V_0 is the volume of the solid at any temperature and pressure relative to its value at $T=0°\text{K}$. Then if one assumes γ_i and σ_i are independent of i, it follows that the volume dependence of a, b, and c are related to n, γ, σ by

$$\begin{aligned} d\ln a/d\ln V&=n(V)=d\log q_0/d\log V, && \text{(A)} \\ d\ln|b|/d\ln V&=2\gamma+\sigma, && \text{(B)} \quad (22) \\ d\ln|c|/d\ln V&=\sigma. && \text{(C)} \end{aligned}$$

The γ introduced here is closely related to Grüneisen's constant. It differs in that a different weighted average over the normal modes is involved in the calculation of the quadrupole splitting and specific heat respectively.

V. ANALYSIS OF EXPERIMENTAL DATA

As already emphasized above, a complete analysis of the data requires that the resonance frequency be known as a function of volume for a series of temperatures. Since, experimentally, the resonance frequency is obtained in the form of ν-*versus*-P isotherms, the equation of state of the solid is required to transform the experimental results into ν-*versus*-V isotherms.

Experimental data representing the equation of state are meager for most solids. While the thermal expansion coefficient is sometimes available, the compressibility has been determined generally at only one or two temperatures, usually above 0°C. Since our measurements extend down to $-77°\text{C}$, it is necessary to have recourse to theory to estimate the form of the $P-V$ isotherms over a wide range of temperature.

In the Appendix a theory is presented which enables the determination of the equation of state,[24] provided the thermal expansion is known experimentally. To a high degree of approximation the compressibility is shown to be a function only of the volume and can be written as

$$\chi(T,V)=-\frac{1}{V}\frac{\partial V}{\partial P}=\frac{V}{V_0}\chi_{00}\Big/\left[1-\zeta\left(\frac{V-V_0}{V_0}\right)\right]. \quad (23)$$

Here V/V_0 is the volume of the solid at any temperature and pressure relative to the volume at $T=0$, $P=0$ atmos; ζ is a constant, different for different solids; whose value is about 3. χ_{00} is the compressibility at absolute zero and $P=0$ atmos. Equation (23) can be integrated at various temperatures, thus producing the equation of state.

The ν-*versus*-V curves can be constructed for each temperature and the ν-*versus*-T curves at constant volume can be analyzed using Eq. (17). From three points on the ν-*versus*-T curves [at temperatures where the approximation of Eq. (17) is valid], a, b', and c' can be found. In principle, this can be done at each volume, thereby yielding a, b', and c' directly as a function of volume. In practice, however, the most accurate technique consists of determining a, b', and c' very carefully at one volume, V_1, and deducing their volume dependence from the volume dependence of ν.

The physical deductions that can be made from the knowledge of $a(V)$, $b(V)$, and $c(V)$ derived from Eqs. (17)–(20) can be divided into two sections which deal with (*A*) the volume dependence, and (B) the absolute magnitudes of a, b, and c.

A-1. The volume dependence $n(V)$ of $q_0(V)$, the static value of the electric field gradient at the nucleus, can be deduced from the volume dependence of a with Eqs. (21A) and (22A).

A-2. The volume dependence γ of the contributing vibration frequencies and the volume dependence σ of

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[24] In what follows it will be helpful to visualize the equation of state as a family of V *versus* P isotherms, each curve being generated by an initial volume fixed by the thermal expansion.

the effective moment of inertia can be deduced from the volume variation of b and c by using Eqs. (19)–(22).

A-3. The relative importance of the volume dependence of q_0 and of the vibration amplitudes on the resonance frequency can be deduced from Eq. (17) as

$$\frac{\partial \ln\nu}{\partial \ln V}=\frac{d\ln a}{d\ln V}+\left[\frac{db}{(d\ln V)}T+\frac{dc}{(d\ln V)}\frac{1}{T}\right]\Big/(1+bT+c/T). \quad (24)$$

$$\frac{\partial \ln\nu}{\partial \ln V}=\frac{d\ln q_0}{d\ln V}+\frac{\partial \ln\nu}{\partial \ln\langle\theta'^2\rangle_{\text{Av}}}\frac{\partial \ln\langle\theta'^2\rangle_{\text{Av}}}{\partial \ln V},$$
$$\langle\theta'^2\rangle_{\text{Av}}\equiv\langle\textstyle\sum_i(\xi_i^0)^2A_i\rangle_{\text{Av}}. \quad (25)$$

This equation shows explicitly how the volume dependence of ν splits into two contributions. The first comes from the volume dependence of q_0, and the second from the volume dependence of the vibration amplitudes. The volume dependence of a, b, and c in Eq. (24) determines the relative importance of these two contributions.

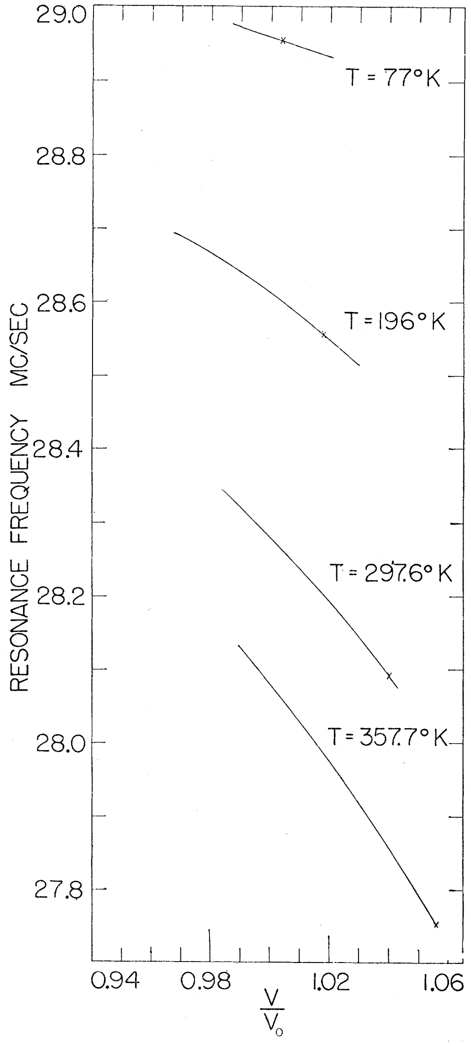

FIG. 7. The ν-*versus*-volume isotherms for $KClO_3$ obtained by using an equation of state. The crosses represent the values of ν at atmospheric pressure.

A-4. Finally, by comparing the curves of the temperature variation of ν at atmospheric pressure with the temperature variation of ν at constant volume ($V/V_0=1$ should be chosen) it is possible to observe directly how much of the change in frequency is due to an explicit temperature variation in the vibration amplitude (Bayer's theory) and how much is due to volume expansion.

B-1. From the absolute magnitude of a, the size of the electric field gradient q_0 can be deduced rather accurately, using Eq. (18), since a can be determined to ±0.05%.

B-2. The absolute magnitude of b and c determines, through Eqs. (19) and (20), the average vibration frequency and the effective moment of inertia $\langle\Theta\rangle$ of those modes which contribute to the sum in Eq. (11). These results can be compared with the experimentally observed Raman lines and theoretical calculations of the moment of inertia of the modes of vibration in order to check the over-all consistency of the physical model on which the theory is based.

1. $KClO_3$

A measurement of the thermal expansion in $KClO_3$ in the range $-195°C<T<21°C$ has been made by Hülsmann and Bilts.[25] The compressibility at room temperature has been determined[26] as $5.0\times10^{-6}/(\text{kg/cm}^2)$ from measurements on a sample in the form

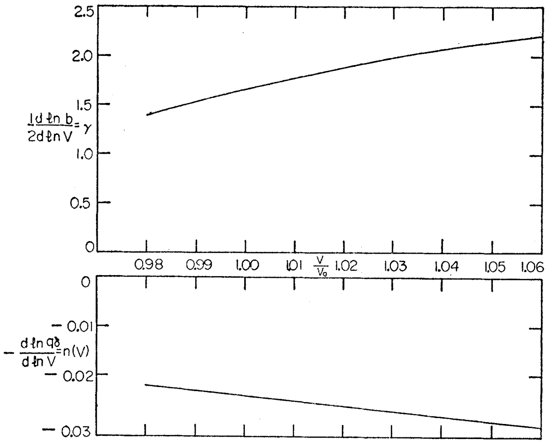

FIG. 8. Upper curve: the volume dependence

$$(\gamma=-\langle\partial \ln\nu_i/\partial \ln V\rangle)$$

of the vibration frequencies for $KClO_3$. Lower curve: the volume dependence of the maximum principal value q_0 of the field gradient tensor for $KClO_3$.

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[25] O. Hülsmann and W. Bilts, Z. anorg. Chem. **219**, 557 (1934).

[26] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

TABLE II. Comparison of ν calculated and observed and $(\partial\nu/\partial P)_{P=0}$ calculated and observed for $KClO_3$.

T °K	ν(calc) Mc/sec	ν(obs) Mc/sec	$(\partial\nu/\partial P)_{P=0}$(calc) cps/kg cm^2	$(\partial\nu/\partial P)_{P=0}$(obs) cps/kg cm^2
357.7	27.751	27.751	38.6	40 ± 3
297.6	28.092	28.093	28.4	29 ± 2
196	28.556	28.556	16.4	15.7 ± 1
77	28.952	28.953	7.6	6.4 ± 0.4

of a compressed slug. With $\zeta=3.33$, Eq. (23) yields $\chi_{00}=4.7\times10^{-6}/(\text{kg/cm}^2)$. With this choice of χ_{00} and ζ, and the known thermal expansion, the equation of state was constructed by integrating Eq. (23). A plot of *ν-versus-V/V*$_0$ for four temperatures, including the 77°K data obtained by Livingston,[19] was made and is shown in Fig. 7. At $V/V_0=1$, a, b, and c were evaluated, using the three lowest temperature isotherms so as to give the most accurate value of c. The volume dependence of a and b was determined from the three highest temperature isotherms because the volume derivatives are most accurately known for these temperatures. The volume variation of c cannot be determined accurately because the volume variation of ν is not known over a wide range of volume at the lowest temperature. From the physical significance of c [Eq. (20)] as the effective moment of inertia of the ClO_3 group (as will be seen later) it is to be expected that c can be considered as independent of volume. The volume dependence $n(V)$ and $\gamma(V)$ derived from a, b, and c, according to the procedure outlined above, is shown in Fig. 8. As a check on the internal consistency of the procedure the temperature dependence of the resonance frequency and its derivative $\partial\nu/\partial P$ for $P=1$ atmos was calculated using Eq. (22). The result agreed extremely well with experiment, as shown in Table II. The complete temperature and pressure variation is therefore well accounted for.

The volume dependence of q_0 is small, since $n\sim0.025$. In $KClO_3$ the field gradient at the position of the Cl^{35} nucleus is produced primarily by ionic and covalency bonding in the ClO_3 group with a few percent ionic contribution from the field set up by the K^+ ion. From n it follows that a 10% decrease in volume will produce a 0.25% increase in q. The ionic contribution of the K^+ ion alone is of this magnitude. (This estimate is made on the basis of Itoh and Kusaka's work on the Na quadrupole coupling in $NaClO_3$.[27]) It must therefore be concluded that the contribution of the ClO_3 group to the volume dependence of q is rather small. This conclusion is consistent with the view that the compression of $KClO_3$ primarily changes the K^+ and ClO_3^- distance while affecting only very slightly the structure of the ClO_3 group. The value of $\gamma(V)$ derived from these experiments is about the same as the value expected for Grüneisen's constant.

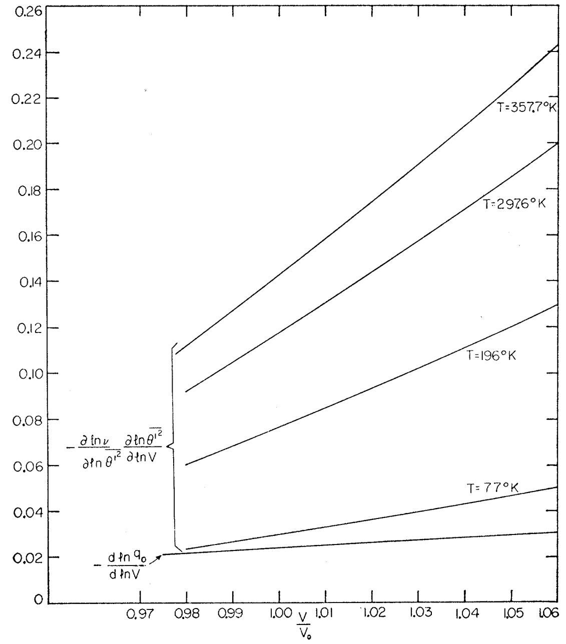

FIG. 9. The contributions of the volume dependence of the lattice vibrations and the volume dependence of q_0 to the volume dependence of the resonance frequency for $KClO_3$, at three different temperatures.

The relative importance of the volume dependence of q_0 and of the vibration amplitudes on the volume dependence of ν can be found from Eq. (24), as explained above. Results are plotted in Fig. 9. From this figure it is seen that at 357°K the volume dependence of the vibration amplitudes contributes about 80% of the observed volume dependence of ν. However, at 77°K the volume dependence of the vibration amplitudes are much smaller, and, as a result q_0 and the vibration amplitudes contribute about equally to the volume dependence of ν.

The separate effects on the frequency ν of the explicit temperature variation of the vibration amplitudes and of the volume variation of q_0 and the vibration amplitudes are seen in Fig. 10. The Bayer curve (B) is a plot of ν as a function of temperature for $V/V_0=1$. It represents the change of the resonance frequency due to the explicit dependence of the vibration amplitudes on the temperature. The difference between the (B) and (A) curves relative to the observed change in frequency from $T=0$ represents the effect of the volume change. At $T=357$°K the volume effect is 25% of the total change in frequency. Curve (C) can be called the Dehmelt[1] curve. In the notation of the present theory it is the extreme high-temperature approximation, i.e., $a+b'T$. The difference between the (B) and (C) curves at temperatures above 80°K represents the effect of the c term.

To conclude the analysis of $KClO_3$ the effective moment of inertia $\langle\Theta\rangle$ and average vibration frequency $\langle\nu\rangle$ were calculated at room temperature and atmos-

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[27] J. Itoh and R. Kusaka, J. Phys. Soc. Japan 9, 434 (1954).

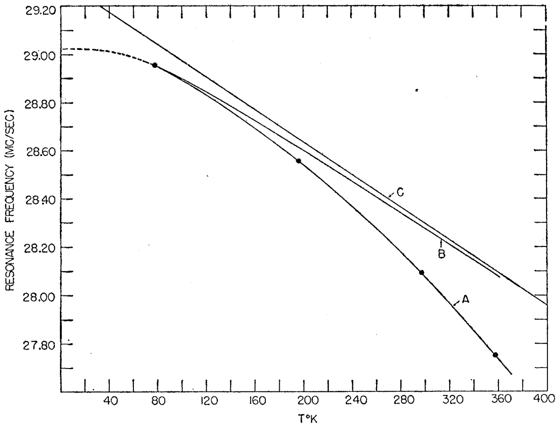

FIG. 10. ν-*versus*-temperature curves for $KClO_3$. Curve (A) is the dependence of ν on temperature at atmospheric pressure as deduced from an analysis of the ν-*versus*-volume isotherms. The circles show the experimental points. The "Bayer curve" (B) shows the dependence of ν on temperature at constant volume ($V/V_0=1$). The "Dehmelt curve" (C) shows ν as a function of temperature in the classical limit.

pheric pressure. It was found that $\langle\nu\rangle=102$ cm^{-1}.[28] Observations of the Raman spectrum[29] show that the lattice frequencies can be split into a high- and low-frequency group. The former corresponds to internal oscillations of the ClO_3 group and can be shown to make little contribution to the temperature dependence of ν.[3] On the other hand, in the low-frequency group, a line at 98 cm^{-1} has been observed which has been identified with the tilting motion of the ClO_3 group as a whole. Such a vibration is just what is required to produce a reduction in the effective value of q. Since the tilting motion can be broken into vibrations around two mutually perpendicular axes, two modes of vibration with about the same moment of inertia and frequency can be expected. Thus, choosing $M=2$ in Eqs. (19) and (20), $\langle\Theta\rangle=84\times10^{-40}$ g cm^2. This is in excellent agreement with the calculated[3] value of $(85\pm2)\times10^{-40}$ g cm^2 for the moment of inertia of the ClO_3 group. The excellent agreement between Θ and ν calculated here, as compared with the Raman data and the theoretical calculation of Θ, must be regarded as somewhat fortuitous, since the contribution from the zero point vibration of the high-frequency modes [$\Omega(T)$ in Eq. (15)] can be expected to be of the order of a few percent of the low-frequency terms.

2. Cu_2O

There exist considerable differences in the literature[30–32] as to the thermal expansion of Cu_2O. All sources agree, however, that the thermal expansion coefficient is very small and that it becomes *negative* at some temperatures. According to Mellor's data, V/V_0 does not change by more than 0.03% in the temperature range $0°C<T<50°C$. In view of this, the thermal expansion was assumed to be negligible over the range of temperature $-77°C<T<100°C$. On the other hand, the compressibility has been measured[33] at 30°C and 75°C on compressed slugs of powdered Cu_2O. The appreciable temperature variation in χ which appears to exist cannot be explained by Eq. (23) in view of the negligible thermal expansion. The graph of Fig. 11 is constructed by choosing the compressibility at $T=196°K$ so that $\partial\nu/\partial(V/V_0)$ is roughly linear with the temperature, as required in Eq. (24). The pressure variation of the compressibility was ignored. From these considerations the equation of state was constructed and a graph (Fig. 12) of ν *versus* V/V_0 was made for three temperatures, including a single point obtained from measurements by Krüger and Berkhout.[34] From ν *versus* T at $V/V_0=1$, a, b, and c were determined. Since, experimentally, ν is a linear function of volume, all results are described accurately by the following equations:

$$a=\{(27.02\pm0.03)-(26\pm1)[(V/V_0)-1]\}\ \text{Mc/sec},$$

$$b=\{-1.29\times10^{-4}+7.62\times10^{-4}[(V/V_0)-1]\}/°\text{K}.$$

As before, the volume dependence of c is not accurately fixed by the data. The value of c at $V/V_0=1$ is $c=-0.074$.

The volume dependence of q is represented by $n=-0.96\pm0.04$. Thus one can say that q depends on the interatomic distances as $\sim1/r^3$. This is exactly what one would expect, if the ionic charge on neighboring O^{--} and Cu^+ ions create the internal electric field. To obtain the correct magnitude of the field gradient at the copper nucleus one has to multiply by an antishielding factor $(1-\gamma_\infty)$, which is about 9 for a Cu^+ ion.[35] If one takes the field gradient produced by the two nearest-neighbor, doubly charged O^{--} ions and multiplies by $(1-\gamma_\infty)$, the correct order of magnitude is obtained for the quadrupole splitting contrary to a previous discussion.[34] A predominantly ionic configuration is therefore consistent with the experimental facts. Clearly, more accurate calculations of q_0, using the ionic model such as those Bersohn[36] carried out for Na^+ in $NaNO_3$ and $NaClO_3$, are desirable for Cu_2O.

A calculation of $d\ln b/d\ln V$ shows that $\gamma-\sigma/2=-2.96$. Since all the interatomic distances are proportional to $V^{\frac{1}{3}}$ in Cu_2O, it follows that $\langle\Theta\rangle\propto(V/V_0)^{\frac{2}{3}}$. Thus, $\sigma=0.666$ and $\gamma=-2.6$. The appearance of a negative value for γ is not inconsistent with Grüneisen's relation, which predicts a negative value for the

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[28] It will be noted that for this value of $\langle\nu\rangle$ and $T=77°K$, $h\nu/kT\sim2$. Since, as shown above, Eq. (14) is rather accurate even for $x=2$, this value of $\langle\nu\rangle$ can be taken as a justification of the use of Eq. (17).

[29] C. Shanta Kumari, Proc. Indian Acad. Sci. **32**, 177 (1950).

[30] O. V. Auwers, Naturwissenschaften **19**, 133 (1931).

[31] R. Uno and T. Okada, J. Phys. Soc. Japan **5**, 23 (1950).

[32] J. W. Mellor, *Inorganic and Theoretical Chemistry* (Longmans, Green and Company, London, 1923), Vol. 3, p. 122.

[33] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **67**, 345 (1932).

[34] H. Krüger and L. Meyer-Berkhout, Z. Physik **132**, 171 (1952).

[35] Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954).

[36] R. Bersohn (private communication); T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

Grüneisen constant of the entire vibration spectrum when the thermal expansion is negative. As mentioned above, the thermal expansion coefficient *is* negative for certain temperatures in Cu_2O.

The relative importance of the volume dependence of q_0 and of the vibration amplitude is shown in Eq. (25), which in the case of Cu_2O takes the form

$$\frac{\partial \ln\nu}{\partial \ln V} \cong -0.96+7.62\times10^{-4}T.$$

The observed *increase* in the volume dependence of ν as the temperature drops results from the opposite signs of the q_0 and $\langle\theta'^2\rangle_{\mathrm{Av}}$ terms. It is clear that the q_0 term is the dominant one. At $T=350$°K the $\langle\theta'^2\rangle_{\mathrm{Av}}$ contribution is only about 25% of the q_0 contribution to the volume dependence of ν.

Despite the strong dependence of the resonance frequency on the volume, the observed temperature variation at atmospheric pressure is almost entirely due to the explicit temperature dependence of $\langle\theta'^2\rangle_{\mathrm{Av}}$ because of the negligible thermal expansion.

The calculated value of the average vibration frequency yields $\langle\nu\rangle=57$ cm^{-1} while $\langle\Theta\rangle=M(138\times10^{-40})$ g cm^2, where M is the number of contributing modes. A calculation of the moment of inertia of the O—CU—O system, assuming these three atoms to be always in a straight line executing oscillations around an axis through the Cu atom perpendicular to the O—Cu—O line, yields a value of 90×10^{-40} g cm^2. No Raman data are available to compare with the deduced value of $\langle\nu\rangle$.

Instead of considering a few vibrations of an O—Cu—O system, it may be more appropriate to consider a complete Debye spectrum of frequencies contributing to the variation of the quadrupole coupling. For temperatures higher than the Debye temperature the analysis based on Eq. (17) remains an excellent approximation. Only the physical interpretation of the $\langle\nu\rangle$ and $\langle\Theta\rangle$ of the preceding paragraph, based on an Einstein model, would have to be modified.

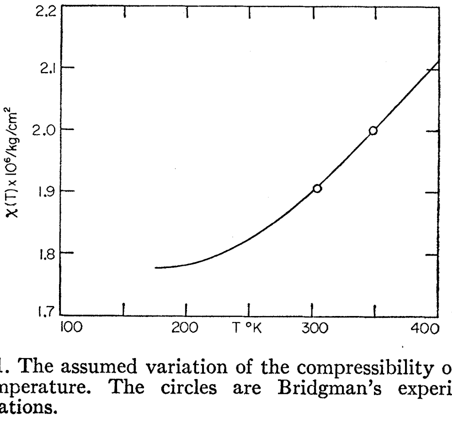

FIG. 11. The assumed variation of the compressibility of Cu_2O with temperature. The circles are Bridgman's experimental determinations.

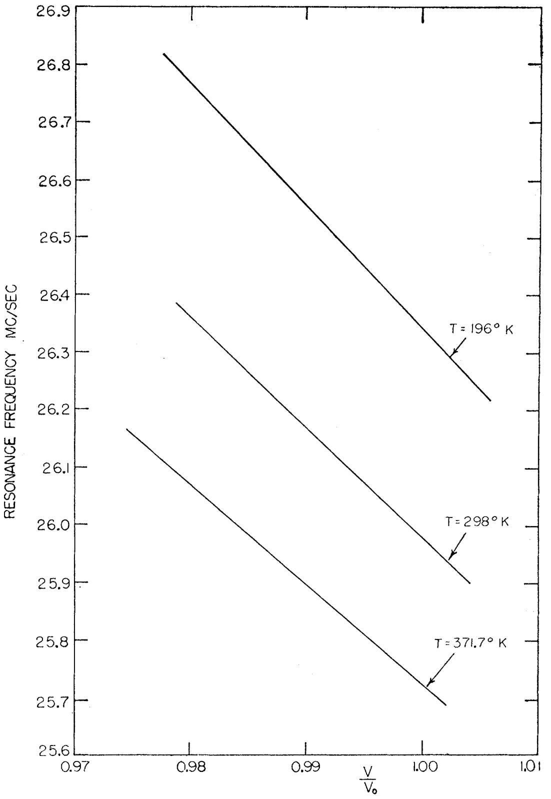

FIG. 12. The ν-*versus*-volume isotherms for Cu_2O. The atmospheric pressure frequencies occur at $V/V_0=1$.

3. Paradichlorobenzene

The behavior of the γ phase of p-$C_6H_4Cl_2$ under pressure requires analysis and explanation despite the absence of information in the literature as to the thermal expansion and compressibility of any of its phases. The compressibility and thermal expansion of nitro-chloro-benzene[37] and phenol,[38] respectively, are known and may be used as a first approximation for α and χ in p-$C_6H_4Cl_2$. The thermal expansion was chosen to be proportional to the temperature and equal to $1.54\times10^{-6}T$ which gives a value of α 30% higher than that of phenol at room temperature. The compressibility was assumed to be 14×10^{-6}/kg cm^2, or about 45% higher than the compressibility of nitro-chloro-benzene at room temperature. For simplicity the temperature and pressure variation of χ was ignored. Keeping in mind the approximate nature of the equation of state, the analysis of the data proceeds with the plot of the three (ν,V) isotherms of the γ phase that are shown in Fig. 13. From the variation of b with volume, one obtains the reasonable results for γ shown in Fig. 14.

In Fig. 15 is plotted the q_0 and $\langle\theta'^2\rangle_{\mathrm{Av}}$ contribution to $\partial \ln\nu/\partial \ln V$. It will be noted that the two contributions

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[37] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).

[38] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1951), p. 2221.

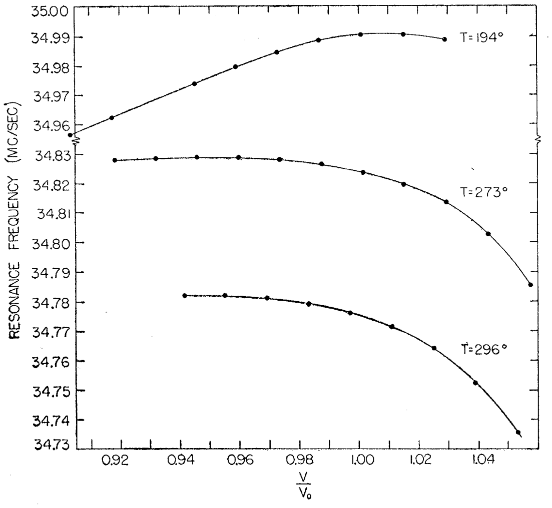

FIG. 13. The *ν-versus*-volume isotherms for the γ phase of paradichlorobenzene.

to the volume dependence of ν are of opposite sign.[39] The upper curve, which is just $n(V)$, shows that the q_0 contribution to $\partial \ln\nu/\partial \ln V$ is primarily a positive and rapidly varying function of the volume. On the other hand, the $\langle\theta'^2\rangle_{\text{Av}}$ contribution is negative and much more weakly dependent on volume. The maximum in the *ν-versus-P* curves comes about as follows: Consider Fig. 15. At low pressure (high volumes) the $\langle\theta'^2\rangle_{\text{Av}}$ contribution dominates, and $\partial \ln\nu/\partial \ln V$ is negative, (thus producing a positive $\partial\nu/\partial P$).[40] As the pressure increases, the q_0 term increases rapidly until it cancels the $\langle\theta'^2\rangle_{\text{Av}}$ term, thereby causing $\partial \ln\nu/\partial \ln V$ to become zero. Above this pressure the q_0 term dominates and $\partial \ln\nu/\partial \ln V$ is positive, signifying a negative $\partial\nu/\partial P$. The maximum shifts to lower pressures as the temperature drops, because the $\langle\theta'^2\rangle_{\text{Av}}$ contribution is smaller at all volumes and hence less pressure is required to cause the q_0 term to dominate.

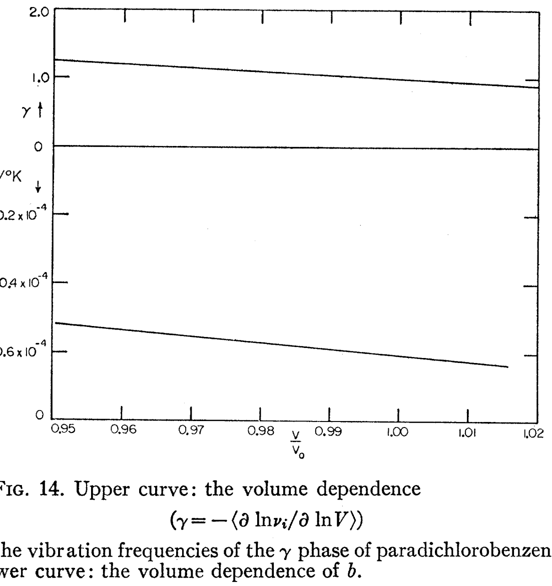

FIG. 14. Upper curve: the volume dependence

$$(\gamma=-\langle\partial \ln\nu_i/\partial \ln V\rangle)$$

of the vibration frequencies of the γ phase of paradichlorobenzene. Lower curve: the volume dependence of b.

The field gradient at the position of the Cl^{35} nucleus is produced primarily by the C–Cl covalent bond. The observed decrease of q_0 with decreasing volume may be regarded as a result of the intermolecular hybridization of the C–Cl bond produced by the close approach of the neighboring molecules. A rather strong variation of the amount of hybridization with volume can be expected in agreement with experiment, but a simple exponential dependence $[n=\text{const}(V/V_0)]$ appears to be too naive. The qualitative behavior of paradichlorobenzene may be typical of covalent molecular crystals.

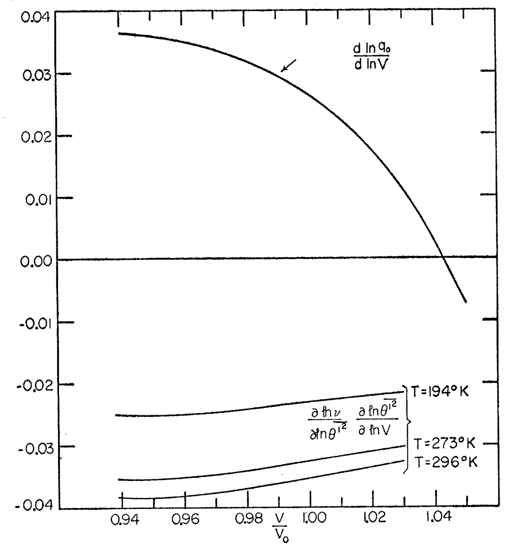

FIG. 15. The contribution of the volume dependence of the lattice vibrations and the volume dependence of q_0 to the volume dependence of the resonance frequency for the γ phase of paradichlorobenzene at three temperatures.

The temperature variation of the resonance frequency of the γ phase is due primarily to the explicit temperature dependence of $\langle\theta'^2\rangle_{\text{Av}}$, the volume effect being small because of the small value of $\partial \ln\nu/\partial \ln V$.

c is not known with sufficient accuracy to permit a determination of $\langle\Theta\rangle$ and $\langle\nu\rangle$ separately. However, the value of b at $V/V_0=1$ is $-0.60\times10^{-4}/°\text{K}$. Using the Raman spectra data[41] for the α phase of paradichlorobenzene, Wang has estimated from two low-frequency modes that $b=-0.71\times10^{-4}/°\text{K}$. While our experi-

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[39] A similar situation occurs for Cu_2O except that there the signs of the two contributions are just the opposite of those observed here.

[40] Since $(1/\nu)(\partial\nu/\partial P)=(\partial \ln\nu/\partial \ln V)(1/V)(\partial V/\partial P)$, a negative value of $\partial \ln\nu/\partial \ln V$ indicates a positive value of $\partial\nu/\partial P$, because $\partial V/\partial P$ is negative.

[41] B. D. Saksena, J. Chem. Phys. 18, 1653 (1950).

mental value of b is closer to the theoretical value than Wang's, this agreement must not be taken too seriously in view of the uncertainties in (1) the equation of state and (2) the contribution of the higher frequency modes to the calculation above. These higher-frequency modes correspond to internal oscillations of the benzene ring.

VI. CONCLUSION

It has been shown above that an understanding of the mechanism of the pure quadrupole splitting requires measurements of ν as a function of temperature and pressure, and a knowledge of the equation of state of the solid. If such information is available, one can deduce the volume dependence of the electric field gradient at the nucleus and also the volume dependence of the vibration frequencies. This deduction has been carried out for three representative solids, $KClO_3$, Cu_2O, and p-$C_6H_4Cl_2$. A theoretical expression for the equation of state of the solid has been developed for use in cases where experimental measurements have not been made. The efficacy of the pure quadrupole resonance in the detection of polymorphic transitions has been demonstrated by the observation of a new high-pressure modification of paradichlorobenzene.

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APPENDIX

The free energy F of a solid with harmonic lattice vibrations is expressed by

$$F=U_{\mathrm{coh}}(V)-kT\sum_{\mu=1}^{3N}\ln 2\sinh\left(\frac{h\nu_\mu(V)}{2kT}\right). \qquad \text{(A-1)}$$

The cohesive energy U_{coh} and eigenfrequencies ν_μ are functions of the volume. The compressibility can be obtained by differentiating (A-1) twice with respect to volume.

$$\frac{1}{\chi V}=\frac{\partial^2 F}{\partial V^2}=\frac{\partial^2 U_{\mathrm{coh}}}{\partial V^2}-\frac{\partial}{\partial V}\left(\frac{\gamma U_{\mathrm{vib}}}{V}\right), \qquad \text{(A-2)}$$

where

$$U_{\mathrm{vib}}=\sum_1^{3N}\frac{h\nu_\mu}{2}\coth\left(\frac{h\nu_\mu}{2kT}\right), \qquad \text{(A-3)}$$

and

$$\gamma=-\left\langle\frac{d\ln\nu_\mu}{d\ln V}\right\rangle=U_{\mathrm{vib}}^{-1}\sum_1^{3N}\left[\frac{h\nu_\mu}{2}\coth\left(\frac{h\nu_\mu}{2kT}\right)\right]\frac{d\ln\nu_\mu}{d\ln V}. \qquad \text{(A-4)}$$

The temperature variation of χ at constant volume is small. This is seen as follows: Assuming γ to be explicitly independent of T, one calculates from Eq. (A-2)

$$\frac{1}{\chi}\left(\frac{\partial\chi}{\partial T}\right)_V\approx\chi\left(\frac{C_v}{V}\right)\gamma\sim 10^{-4}. \qquad \text{(A-5)}$$

The observed dependence on temperature at constant pressure is mostly due to thermal expansion, and the explicit temperature dependence calculated in Eq. (A-5) will henceforth be neglected. Expanding Eq. (A-2) around the equilibrium volume V_0 at absolute zero of temperature and zero pressure, one finds

$$\frac{1}{\chi V}=\frac{1}{\chi_{00}V_0}+\left(\frac{\partial^3 U_{\mathrm{coh}}}{\partial V^3}\right)_{V=V_0}(V-V_0)-\left[\frac{\partial^2}{\partial V^2}\left(\frac{U_{\mathrm{vib}}\gamma}{V}\right)\right](V-V_0).$$

Even at 300°K the contribution of the last term is usually small compared to the second term on the left-hand side, and to a good approximation one may write at all temperatures of interest

$$\chi(T,V)=\frac{V_0}{V}\chi_{00}\Big/\left[1-\zeta\left(\frac{V-V_0}{V_0}\right)\right]. \qquad \text{(A-6)}$$

with the constant ζ defined by

$$\zeta=-V_0\chi_{00}\left(\frac{\partial^3 U_{\mathrm{coh}}}{\partial V^3}\right)_{V=V_0}. \qquad \text{(A-7)}$$

From the volume expansion as a function of temperature at atmospheric pressure, Eq. (A-6) gives directly the compressibility at atmospheric pressure. Furthermore, an integration of Eq. (A-6) gives directly the detailed shape of the (P,V) isotherms.

ζ can be evaluated from the thermal expansion and the temperature variation of χ at constant pressure. This yields a value of ζ between 3 and 9 for most experimentally investigated solids.[42] ζ can also be found from the shape of the (P,V) isotherms at any temperature. From the semiempirical Birch-Murnaghan law which serves as a good representation of the (P,V) isotherms for a wide range of solids,[42] one can deduce $\zeta=3.33$.

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[42] F. Birch, J. Geophys. Research **57**, 227 (1952).