[†] Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corp.

[1] W. A. Sibley, E. Sonder, and C. T. Butler, Phys. Rev. 136, A537 (1964).

[2] M. Ikeya, N. Itoh, T. Okada, and T. Suita, J. Phys. Soc. Japan 21, 1304 (1966).

[3] K. Thommen, Phys. Letters 2, 189 (1962).

[4] E. Sonder and L. C. Templeton, Phys. Rev. 164, 1106 (1967).

[5] E. Sonder and W. A. Sibley, Phys. Rev. 129, 1578 (1963).

[6] P. G. Harrison, Phys. Rev. 131, 2505 (1963).

[7] We shall be using the following nomenclature in this paper: Vacancy refers to all vacancies, irrespective of charge state; F center refers to a vacancy containing one electron and being uncharged *with respect to the normal crystal*. F^+ and F^- centers are vacancies that are, respectively, one electronic charge more positive or more negative than F centers. F_2 centers are two F centers in adjacent lattice sites.

[8] H. Rabin, Phys. Rev. 129, 129 (1963).

[9] J. Nahum, Phys. Rev. 174, 1000 (1968).

[10] R. Onaka, I. Fujita, and A. Fukada, J. Phys. Soc. Japan, Suppl. 18, 263 (1963).

[11] T. Maysuyama and M. Hirai, J. Phys. Soc. Japan 27, 1526 (1969).

[12] D. K. Dawson and D. Pooley, Solid State Commun. 7, 1001 (1969).

[13] J. D. Comins and P. T. Wedepohl, Solid State Commun. 4, 537 (1966).

[14] G. Horn and H. Peisl, Z. Physik 194, 219 (1966).

[15] C. H. Seager, D. O. Welch, and B. S. H. Royce, International Symposium on Color Centers in Alkali Halides, Rome, 1968 (unpublished).

[16] D. Pooley, Proc. Phys. Soc. (London) 89, 723 (1966).

[17] F. J. Keller and R. B. Murray, Phys. Rev. Letters 15, 198 (1965).

[18] L. A. Pung and Yu Yu Khaldre, Bull. Acad. Sci. USSR 30, 1507 (1966).

[19] R. B. Murray, H. B. Dietrich, and F. J. Keller, J. Phys. Chem. Solids 31, 1185 (1970).

[20] C. L. Bauer and R. Gordon, Phys. Rev. 126, 73 (1962).

[21] C. B. Lushchik, G. K. Vale, E. R. Ilmas, N. S. Rooze, A. A. Elango, and M. A. Elango, Opt. i Spektroskopiya 21, 686 (1966) [Opt. Spectry. (USSR) 21, 377 (1966)].

[22] D. W. Lynch and D. A. Robinson, Phys. Rev. 174, 1050 (1968).

[23] We have not been able to measure the ultraviolet absorption band (α band) of empty negative-ion vacancies (F^+ centers). Previous experience with undoped KCl [E. Sonder and W. A. Sibley, Phys. Rev. 140, A539 (1965); and other (unpublished) work] has shown that the predominant vacancy form produced by irradiation above approximately 40 °K is the F center and that about 20% of the vacancies appear as F^- and F^+ centers. Also, in KCl bleaching of F^- centers removes F^+ centers as well. Our claim in this work, that we are observing the total vacancy concentration, rests on the assumption that NaCl behaves similarly to KCl.

[24] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters 7, 57 (1961).

[25] Trapped-hole annealing has been analyzed for KI and KCl. For KI, the $[I_2^-]$ band disappears near 100 °K with an activation energy of 0.28 eV [F. J. Keller and R. B. Murray, Phys. Rev. 150, 670 (1966)]; for KCl, the $[Cl_2^-]$ band disappears near 200 °K with an activation energy of 0.53 eV [T. J. Neubert and T. A. Reffner, J. Chem. Phys. 36, 2780 (1962)]. It is reasonable to assume that trapped-hole annealing in the different alkali halides occurs by a similar process so that the preexponential factor A, in the rate expression $Ae^{-E/kT}$, is of the same magnitude in the various alkali halides. It follows then that the activation energy E is proportional to annealing temperature, permitting us to estimate that the activation energy for NaCl, where the trapped hole disappears near 160 °K, is approximately 0.4 eV.

[26] We assume that the average energy per electron-hole pair is twice the band gap or ~ 15 eV.

[27] Y. Farge, M. Lambert, and R. Smoluchowski, Solid State Commun. 4, 333 (1966).

[28] E. Sonder and L. C. Templeton, Phys. Rev. 164, 1106 (1967).

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Pressure-Induced Phase Transitions in Solids: BaF_2†

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(Received 11 June 1970)

Similarities between the pressure dependences of the elastic constants of BaF_2 and RbI suggested that a pressure-induced phase transition should obtain in BaF_2. This transition has been observed. With increasing pressure at 295 °K the transition occurs at 26.8 kbar. The transition pressure decreases with increasing temperature, and at sufficiently high pressure the transition can be induced by raising the temperature. The possible lattice dynamical nature of the transitions in RbI and BaF_2 is discussed.

I. INTRODUCTION

The study of phase transitions in solids and the interpretation of such transitions in terms of the dynamics of the crystal lattice are of prime importance. The general conditions for lattice stability are discussed by Born and Huang.[1] One distinguishes between stability with respect to (i) homogeneous deformations (i.e., long-wavelength modes) and (ii) small deformations. In either case, the limit of stability against a particular mode is approached as the corresponding frequency decreases and approaches zero.

This connection between lattice stability and the behavior of the normal modes has received much recent attention, especially in connection with ferroelectric and antiferroelectric crystals where there is now direct experimental evidence that the transitions which occur in such crystals are associated with the softening of the frequencies of certain lattice vibrational modes.[2] Much less has been done on an important class of phase transitions which occur in relatively simple ionic crystals. The best example of this type is the NaCl → CsCl (structure types) transition which occurs in several of the alkali halides with either increasing temperature (e.g., the CsCl → NaCl transition in CsCl) or increasing pressure (e.g., the NaCl → CsCl transition in RbI and KCl). Of these, the pressure-induced transition in RbI has received the most attention, and certain speculations concerning its lattice dynamical origin have been made (as discussed later).

Recent studies[3] of the effects of pressure on the elastic constants of CaF_2 and BaF_2 have shown that for BaF_2 a number of key features are qualitatively similar to those observed in similar measurements on RbI. These features suggested to us that a pressure-induced transition should obtain in BaF_2. We have since observed such a transition.[4] After completion of the present work a paper by Dandekar and Jamieson appeared[5] in which evidence is reported for pressure-induced transition in BaF_2 as well as CaF_2 and SrF_2. The evidence is based on high-pressure x-ray diffraction measurements utilizing a Bridgman anvil apparatus. The transition pressures were not accurately determined. It was also brought to our attention that evidence for a phase transition in BaF_2 was reported by Minomura and Drickamer[6] from optical high-pressure measurements. In the present paper we shall (i) outline the available evidence based on elastic constants which suggested the transition, (ii) present the experimental results, and (iii) discuss the possible lattice dynamical origin of the transitions in RbI and BaF_2.

II. PRESSURE DEPENDENCE OF ELASTIC CONSTANTS

Table I shows the logarithmic pressure derivatives for several elastic constants for BaF_2 and RbI. Similar results for CaF_2 and NaCl are listed for comparison. Also shown are the corresponding so-called "mode γ's" defined by

$$\gamma_i \equiv -\frac{d \ln \nu_i}{d \ln V}\,, \tag{1}$$

where ν_i is the mode frequency and V is the volume. The γ_i's are related to the Grüneisen parameter and express the effect of dilation of the lattice on the frequencies of the various modes. They are simply obtained from the known pressure derivatives of the elastic constants and the volume compressibility.[7]

Examination of the data in Table I reveals the following: (i) For the alkali halides, $(d \ln C_{44}/dP)$ and the corresponding $\gamma(C_{44})$ are small, and they are negative for RbI. Negative values of these quantities imply a softening (i.e., decrease of stability) of the lattice under compression with respect to deformation of the C_{44} type. RbI transforms from the NaCl to the CsCl structure at ~4.0 kbar.

(ii) For CaF_2 and BaF_2, $(d \ln C'/dP)$ and the corresponding $\gamma(C')$ are small, and they are negative for BaF_2. C' is one of the shear constants for wave propagation in the [110] direction, the other shear constant being C_{44}.

The significance of these observations is the more important for the present purposes because the property of the C' constant in the fluorite (i.e., CaF_2-type) lattice, in which BaF_2 crystallizes, resembles that of the C_{44} constant in the NaCl lattice.[3] The relative displacements between near neighbors associated with C' of CaF_2 and C_{44} of NaCl are somewhat similar.

One further related observation is of interest. The temperature dependence of the elastic constants at constant pressure is made up of the sum of a pure temperature (i.e., volume-independent) contribution and a pure volume contribution, i.e.,

$$\left(\frac{d \ln C_{ii}}{dT}\right)_P = \left(\frac{d \ln C_{ii}}{dT}\right)_V + \alpha \left(\frac{d \ln C_{ii}}{d \ln V}\right)_T\,, \tag{2}$$

TABLE I. Values of the logarithmic pressure derivatives (in units of 10^{-3} kbar^{-1}) and the corresponding mode γ's for several adiabatic elastic constants of NaCl, RbI, CaF_2, and BaF_2. C'_{11} and C' are, respectively, the longitudinal and one of the shear constants for propagation in the [110] direction, and the notation is $C'_{11} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ and $C' = \frac{1}{2}(C_{11} - C_{12})$.

	NaCl[a]	RbI[b]	CaF_2[c]	BaF_2[c]
$(d \ln C_{11}/dP)$	23.9	52.5	3.69	5.24
$\gamma(C_{11})$	2.62	2.61	1.34	1.32
$(d \ln C_{44}/dP)$	2.9	−17.8	3.90	3.03
$\gamma(C_{44})$	0.17	− 1.13	1.43	0.69
$(d \ln C'_{11}/dP)$	16.6	39.5	4.73	6.24
$\gamma(C'_{11})$	1.78	1.43	1.76	1.61
$(d \ln C'/dP)$	26.3	55.5	1.42	−0.70
$\gamma(C')$	2.91	2.77	0.41	−0.36

[a] Values taken from R. A. Bartels and D. E. Schuele, J. Phys. Chem. Solids 26, 537 (1965).

[b] Values calculated from data in Refs. 7 and 15.

[c] Values taken from Ref. 3.

where α is the volume thermal-expansion coefficient. Unlike the case for the other C_{ij}'s in Table I, for both C_{44} of RbI and C' of BaF_2 the measured quantity[3,7] $(d \ln C_{ij}/dT)_P$ is largely determined by the volume-independent contribution $(d \ln C_{ij}/dT)_V$. This latter contribution arises from anharmonic effects, which thus play an important role in deformations of the C_{44} type in RbI and the C' type in BaF_2.

The above-mentioned similarities in the elastic properties of RbI and BaF_2 motivated the search for the pressure-induced transition in BaF_2 which was observed in this work.

III. EXPERIMENT AND RESULTS

The transition was studied by measuring the change in the dielectric constant (capacitance) and dielectric loss of BaF_2 samples as functions of pressure and temperature. Samples were in the form of slabs (0.5–1.0) cm^2×(0.05–0.07) cm thick cut from a large single crystal obtained from the Harshaw Chemical Co. Aluminum electrodes were deposited on the large sample faces by evaporation in vacuum. The measurements were made in a 30-kbar hydrostatic pressure apparatus using a 50 : 50 mixture of n-pentane and isopentane as pressure fluid. The details of the techniques including pressure calibration were similar to those described earlier.[8] Pressure was measured to an accuracy > ± 1%.

The change in sample capacitance with pressure at 295 °K is shown in Fig. 1. A discontinuous increase in capacitance as well as a large increase in the dielectric loss by a factor > 10^3 (not shown) accompany the transition which is observed at 26.8 kbar. The dielectric constant decreases with increasing pressure in both the low-pressure and high-pressure phases, and the transition is characterized by a large hysteresis as shown. Our earlier results on RbI are shown in Fig. 1 for comparison, and again strong similarities are observed. Measurements on BaF_2 were also made at elevated temperatures, and above a certain pressure the transition can be induced by raising the temperature. The transition pressure P_t decreases with increasing temperature as shown in Fig. 2. The open circles represent data taken with increasing pressure at constant temperature, and the dark circles represent data taken with increasing temperature at constant pressure. The hysteresis between forward and reverse transition decreases with increasing temperature. For example, it has a value of ~ 18 kbar at 22 °C and ~ 12.5 kbar at 150 °C. The average slope dP_t/dT (for forward and reverse transitions) is $\approx -2.6\times10^{-2}$ kbar/°K below 100 °C and $\approx -2.2\times10^{-2}$ kbar/°K between 100 and 300 °C. The insert in Fig. 2 shows a schematic temperature-pressure phase diagram for BaF_2.

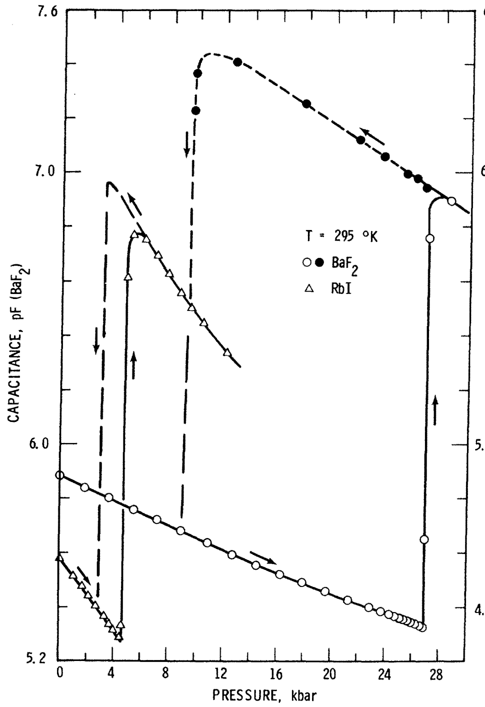

FIG. 1. Pressure dependence of the static dielectric constant (capacitance) of BaF_2 showing the first-order phase transition at 26.8 kbar and the large hysteresis associated with the transition. Similar measurements on RbI are shown for comparison.

The transition in BaF_2 is from the cubic-fluorite structure to the orthorhombic α-$PbCl_2$ structure.[5] Both structures contain four molecules per unit cell. In the fluorite structure (space group $Fm3m - O_h^5$) each fluorine ion is tetrahedrally surrounded by four barium ions, and each barium ion is at the center of a cube of eight equally distant fluorine ions. In the high-pressure orthorhombic phase (space group $Pbnm$-V_h^{16}) the coordination is difficult to define as the structure is quite distorted. For example, each barium has nine fluorine neighbors, but the distances are not all equal.[9] There is a large volume change at the transition with $\Delta V/V_{\text{cubic}} \approx -0.11$ at room temperature.[5] Since the transition is of first order, use of this volume change along with the above value of dP_t/dT allows us to estimate the entropy change from the Clapeyron equation

$$\frac{dP_t}{dT} = \frac{\Delta S}{\Delta V} . \tag{3}$$

Based on an initial (1 bar) volume $V_0 = 0.207$ cm^3/g and compressibility $\kappa = 1.73\times10^{-3}$ kbar^{-1}, the volume change at the transition is found to be $\Delta V \approx -0.022$ cm^3/g. Using this value of ΔV and the initial slope $dP_t/dT \approx -2.6\times10^{-2}$ kbar/°K in Eq. (3) yields $\Delta S \approx 2.4$ cal/g mole °K.

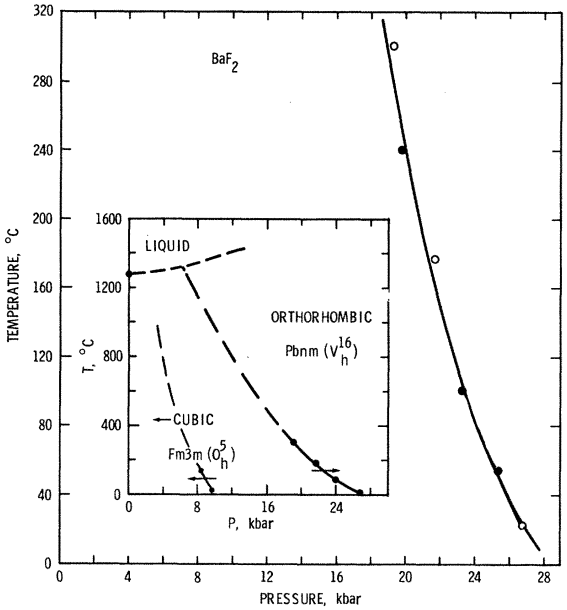

FIG. 2. Temperature dependence of the transition pressure of BaF_2. The data were taken with increasing pressure at constant temperature (open circles) and with increasing temperature at constant pressure (closed circles). The insert shows a schematic temperature-pressure phase diagram for BaF_2 where the dashed lines are sketched in. The pressure hysteresis of the transition decreases with increasing temperature.

IV. DISCUSSION

We now turn to a discussion of the nature of the transitions in RbI and BaF_2. The usual macroscopic description of such transitions in terms of the difference between the free energies of the two phases (the one with the lower free energy being stable) although very important, does not provide any insight into the microscopic nature of the instability. However, the free energy can, in principle, be expressed in terms of the atomic parameters which occur in the theory of lattice dynamics. Some lattice dynamical considerations of the phase transitions in an anharmonic crystal have been treated by a number of authors.[10] For the simple case of a displacive transition the difference between the free energies of the two phases is (using Cowley's notation[10]) given by

$$\Delta F=\sum_{jj'}\eta(\vec{q}j)\eta^*(\vec{q}j')\times[\omega(\vec{q}j)^2\delta_{jj'}+2\omega(\vec{q}j)D(\vec{q}jj',\ \Omega=0)]\ , \qquad (4)$$

where $\omega(\vec{q}j)$ is the harmonic frequency of the normal mode of wave vector $\vec{q}$ in the jth branch; $D(\vec{q}jj', \Omega=0)$ is the anharmonic contribution to the self-energy of the phonons which is a complicated function of the phonon frequencies and occupation numbers and of the thermal strain; Ω is the applied frequency; $\eta(\vec{q}j)$ is the normal coordinate which specifies the deformation. It is defined in terms of the displacement $\vec{u}(l,k)$ of the kth atom in the lth cell from the equilibrium position by

$$\vec{u}(l,k)=(Nm_k)^{-1/2}\sum_{\vec{q}j}\eta(\vec{q}j)\,\vec{e}_k(\vec{q}j)\,e^{i\vec{q}\cdot\vec{R}(l,k)}\ . \qquad (5)$$

Here N is the number of unit cells per unit volume, m_k is the mass, $\vec{e}_k(\vec{q}j)$ is the polarization vector, and $\vec{R}(l,k)$ is the position vector of the kth atom. Coupling between the normal modes and the external strains introduces extra terms into the free energy, and the strength of this coupling determines whether the transition is first or second order.[10]

Buerger[11] proposed a mechanism whereby the NaCl → CsCl transition results from instability with respect to finite strain along a [111] direction. But, because C_{44} decreases by only ~10% up to the transition pressure in RbI, Daniels and Smith[7] argued against such a mechanism and instead put forth the hypothesis that the NaCl structure becomes unstable by the vanishing of one of the short-wavelength lattice frequencies in a mode of the C_{44} type. In particular, they postulated that the frequency of the transverse acoustic (TA) phonon at the [100] zone boundary (ZB) should vanish at the transition pressure. Theoretical calculations of the dispersion relations of RbI by Hardy and Karo[12] have shown that for certain choice of the model parameters and by including some short-range three-body interactions such an instability can obtain under pressure.

In order to test these predictions, Saunderson[13] measured the effect of pressure on the frequency $\nu\equiv\omega/2\pi$ of the [100] TA ZB phonon in RbI by inelastic scattering of neutrons. A decrease in ν of $(3.45\pm0.22)\%$ kbar, or ~14% up to the transition pressure, was observed. Since this is "clearly far short of the 100% (decrease) required for instability," this result was interpreted as *not* supporting the Daniels and Smith hypothesis. Daniels[14] arrived at the same conclusion on the basis of Hardy and Karo's results and low-temperature thermal-expansion data.

It should be pointed out that the above considerations concerning ν and C_{44} overlook a very important point, and that is the transition in RbI (as is also true of BaF_2) is strongly first order, and thus there is no requirement that a soft mode frequency precisely vanishes in order for a transition to take place. Theoretical considerations[10] show that it is only for a second-order transition that the frequency $\omega(\vec{q}j)$ of the pertinent mode vanishes at the transition and, furthermore, for such a transition only one normal mode of a certain $(\vec{q}j)$ can be involved. In a first-order transition, on the other hand, generally more than one mode may be involved and none of their frequencies vanish at the transition. Although the details of the theory of first-order transitions incorporating large homogeneous strain are complex, the available theory[10] suggests that unless the frequencies of the pertinent modes are low, these modes will yield large positive contributions to the free energy [see Eq. (4)], and this does not favor the transition.

In view of the above, two features of Saunderson's results stand out. First is the low value of ν_{TA} at the [100] ZB, namely, 0.67×10^{12} Hz at 1 bar. This is also shown up in Hardy and Karo's calculations and the more recent calculation by Barsch and Achar.[15] Second is the large decrease (~3.5%/kbar) of this frequency with pressure. These features suggest to us that even though another mode (or modes) may be involved, the softening of the [100] TA ZB mode with pressure plays an important role in the transition in RbI. It is of particular interest to note that Barsch and Achar's calculations show that for RbI the mode γ associated with the [100] longitudinal-acoustic (LA) ZB mode is also negative ($\gamma = -1.34$), indicating a decrease with increasing pressure in the stability of the lattice with respect to this mode. (All the optical mode γ's are positive.) Thus we have the strong indication that both the [100] TA and LA ZB modes are involved in the RbI transition. That this may indeed be the case has been pointed out by Barsch[16] who finds that the ionic displacements involved in the NaCl → CsCl transition can be described in terms of the displacements associated with the two above-mentioned modes.

The similarities between BaF_2 and RbI discussed earlier suggest, by analogy, that in the case of BaF_2 the softening of the frequencies of the [110] TA phonon branch, particularly the ZB mode, may be important in the transition in this crystal. If so, the frequency of this mode should be low and should decrease with pressure. Other modes must also be involved. The large pressure and temperature hysteresis between forward and reverse transitions in BaF_2 (and similarly in RbI) are indicative of the fact that considerable activation energy is involved. It should be remembered, however, that the activation energy influences only the kinetic of the transition. The driving force for the transition is the difference between the free energies of the two phases [as is given for example by Eq. (4)] and is independent of the activation energy.

Finally, one further observation can be made. The data in Table I show that the quantities $(d\ln C_{44}/dP)$ and $\gamma(C_{44})$ for NaCl and $(d\ln C'/dP)$ and $\gamma(C')$ for CaF_2 are quite small, but positive. Since there is evidence[5,17] that these crystals undergo pressure-induced transitions at sufficiently high pressure (> 80–100 kbar), we suspect that the above quantities should change from positive to negative with increasing pressure. The extension of the elastic-constant measurements to higher pressures should be most interesting.

ACKNOWLEDGMENTS

I wish to thank W. L. Chrisman for assistance in some of the experimental details and Professor Dandekar for bringing to my attention the work in Ref. 5.

[†] Work supported by the U. S. Atomic Energy Commission.

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Cambridge, England, 1954). For a more recent account see D. C. Wallace, in *Advances in Materials Research*, edited by H. Herman (Interscience, New York, 1968), Vol. 3, p. 331.

[2] See, e.g., G. Shirane and Y. Yamada, Phys. Rev. 177, 858 (1969); 177, 848 (1969) and references therein.

[3] C. Wong and D. E. Schuele, J. Phys. Chem. Solids 29, 1309 (1968).

[4] P. W. Bridgman's shearing measurements to ~ 50 kbar on polycrystalline samples of BaF_2, SrF_2, and CaF_2 [Proc. Am. Acad. Arts Sci. 71, 387 (1937)] did not show any evidence of phase transitions in these compounds.

[5] D. P. Dandekar and J. C. Jamieson, Trans. Amer. Crystallogr. Ass. 5, 19 (1969).

[6] S. Minomura and H. G. Drickamer, J. Chem. Phys. 34, 670 (1961).

[7] W. B. Daniels and C. S. Smith, *Physics and Chemistry of High Pressures* (Society of Chemical Industry, London, 1963), p. 50.

[8] G. A. Samara, J. Phys. Chem. Solids 26, 121 (1965).

[9] R. W. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. 1, Chap. IV.

[10] R. A. Cowley, Phil. Mag. 11, 673 (1965); P. C. Kwok and P. B. Miller, Phys. Rev. 151, 387 (1966).

[11] M. J. Buerger, in *Phase Transformation in Solids*, edited by R. Smoluchowski, J. E. Mayer, and W. A. Weyl (Wiley, New York, 1958), p. 183.

[12] J. R. Hardy and A. M. Karo, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 195.

[13] D. H. Saunderson, Phys. Rev. Letters 17, 530 (1966).

[14] W. B. Daniels, J. Phys. Chem. Solids 28, 350 (1967).

[15] G. R. Barsch and B. N. N. Achar, Phys. Status Solidi 35, 881 (1969).

[16] G. R. Barsch (unpublished).

[17] W. A. Bassett, T. Takahashi, H. Mao, and J. S. Weaver, J. Appl. Phys. 39, 319 (1968).