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Sound velocities and dielectric losses of Ag_2HgI_4 in the vicinity of the phase transition

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We observed an anomaly in the velocity of longitudinal sound waves at the 51°C order-disorder phase transition of Ag_2HgI_4, but not in the velocity of transverse waves. We found two relaxation peaks in the dielectric losses above the transition temperature; only one relaxation appears in the low-temperature phase. We interpret the anomaly in the sound velocity as due to a linear coupling between the order parameter and the volume change. We find a Debye temperature of 82°K. The observation of the dielectric relaxations favors a model of electrical conduction with thermal-activated motion of Ag^+ ions in contrast to the proposed polaron model for Ag_4RbI_5, in which the Ag^+ ions are free to move in the lattice.

I. INTRODUCTION

The compound silver mercuric iodide (Ag_2HgI_4) exhibits a first-order transition with a large change in its electrical conductivity at 51°C.[1,2] It belongs to the large class of materials known as superionic materials.[3] Most of the recent investigations on the properties of this compound deal with the electrical conductivity as a function of temperature[4] and pressure[2,5] and with structure determinations.[6] Thermal studies have also been performed by Ketelaar.[7] In this paper, we present measurements which give new information on the properties of Ag_2HgI_4: sound velocities and dielectric losses.

At a phase transition, one generally expects to observe anomalies in the elastic constants because of the interaction between the long-wavelength phonons and the mechanism which induces the phase transition. However, at a phase transition not all the elastic constants are affected in the same manner[8] and their behavior can add further insight on the transition process. In particular, one can deduce from elastic measurements the form of this interaction. In our case, the order parameter η which is a scalar, can be related to the ordering of the Ag ions. Rehwald[9] predicted that in such a case a linear coupling of the order parameter takes place only with the volume change δ. Coupling with the shear is not linear and is generally not very important.

It is important to note that among the superionic conductors, one can find two types of phase transitions, labeled by Pardee and Mahan,[10] class-I and class-II transitions. The class-I transitions are characterized by a large discontinuity in the electric conductivity and they are of first order. The class-II transitions are of second order (divergence of the specific heat) and the ionic conductivity is continuous with a change in the activation energy. Some materials exhibit only a class-II transition like $C_5H_6NAg_5I_6$ or CaF_2 (see references in Ref. 10). Others have both class-I and class-II transitions, but the class-I transition occurs always at a lower temperature than that of the class-II transition. (Example: AgI, $T_1 = 144°C$ and $T_2 = 430°C$, $RbAg_4I_5$, $T_1 = -150°C$ and $T_2 = -64°C$.) Ag_2HgI_4 is one example of a material having only class-I transition.

The nature of the two transitions is still under discussion, but there is agreement that they are connected to the release of the moving ions.

Acoustic measurements have been made on $RbAg_4I_5$,[11,12] but only at the class-II transition. All the elastic constants showed discontinuities and there was a large increase of the attenuation for the transverse acoustic waves at the transition temperature. In this paper, we present the first acoustic measurement at a class-I transition, which is the only one observed in Ag_2HgI_4 (Pardee and Mahan[12] predicted that a class-II transition must also exist in Ag_2HgI_4). As we shall see the acoustic behavior observed at the class-I transition of Ag_2HgI_4 is very different from that observed at the class-II transition of $RbAg_4I_5$.

Previously, the electrical conductivity of Ag_2HgI_4 had only been measured at dc or low-frequency ac.[1,2,4,5,13] From their careful measurements on single crystals Browall and Kasper[4] concluded that the mobile ions Ag^+ have a thermal-activated motion similar to other, normal, ionic conductors like AgCl and AgBr, as opposed to the superionic conductors like AgI and Ag_4RbI_5. In these compounds it is assumed that the mobile ions are free to move and the polaron model has been used[10,14] to account for the conductivity. We set out to make measurements of the dielectric losses a function of frequency to verify the conclusions of Browall and Kasper.

II. EXPERIMENTAL

The samples were prepared as outlined in Ref. 2 from Ag_2HgI_4 powder furnished by K and K Laboratories (Plainview, N.Y.). The polycrystalline samples were cylinders of 1 cm diam. For the elastic measurements the thickness was about 3 mm, and for the dielectric measurements it was reduced to 1 mm. The density of the different samples varied between 5.96 and 5.93 g/cm^3, which can be compared to the x-ray-determined density[13] 6.078 g/cm^3.

The sound velocities were measured at 10 MHz by the cw resonance method of Bolef and Menes.[15] This method has the advantage of simplicity since the experimental arrangement consists of a Q-meter and a digital frequency meter. The precision of this method is comparable to that of the pulse-echo technique. In the present case, the main difficulty was to get samples with good polished surfaces and precise parallelism of the faces. This difficulty was due to the softness and friability of the polycrystalline samples. The bond to the piezoelectric quartz transducer was made with vacuum-pump oil for measurement of the longitudinal wave velocities and with wax for the transverse waves. The absolute accuracy of the measurements was about 4%, but the relative precision was about 1.5%. Because of the difficulty mentioned, we did not get sharp peaks in the resonance of the composite oscillator (quartz plus sample) and this was the main limitation to the precision.

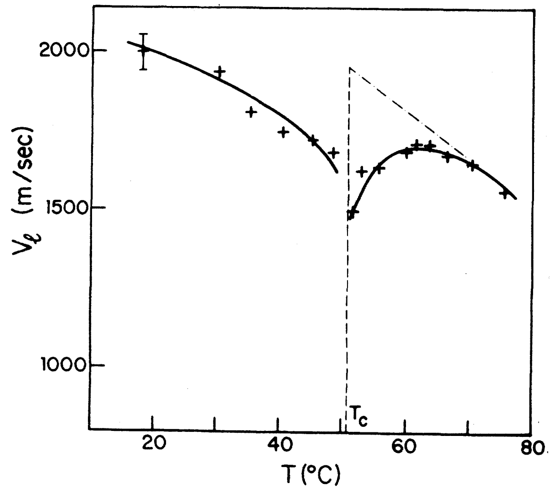

FIG. 1. Velocity of the longitudinal waves of polycrystalline Ag_2HgI_4 as a function of T. The dashed line indicates the extrapolated values of V_l if there was no phase transition. The continuous line corresponds to a visual fit. The bar shows the error.

The dielectric losses were also measured with the Q-meter between 0.25 and 50 MHz. We used a small furnace to change the sample temperature which was stabilized within ±0.1°C.

III. EXPERIMENTAL RESULTS

A. Sound velocities

In Fig. 1, we present the variation of the longitudinal wave velocity V_l with the temperature T. Note: the decrease of V_l in the low-temperature phase and the slight discontinuity at 50°C; however, the results are also consistent with a continuous curve, exhibiting a discontinuity in the slope. In the high-temperature phase V_l begins to increase and above 60°C it decreases again. The values of V_l are relatively low, being 2000 m/sec at room temperature. From this we calculated the bulk modulus at room temperature to be $(2.4 \pm 0.2) \times 10^{11}$ dyn/cm^2.

The velocity V_t of the transverse waves was measured accurately only at room temperature and we obtained $V_t = 810$ m/sec. Above room temperature, the results we obtained were less precise. Nevertheless, we can say that V_t is practically temperature independent and in particular that the discontinuity in V_t, if any, is small.

From the values of V_t and V_l, we can calculate the Debye temperature at room temperature using the formula[16]

$$\Theta = \frac{h}{k}\left(\frac{9n}{4}\right)^{1/3}\left(\frac{1}{V_l^3}+\frac{2}{V_t^3}\right)^{-1/3},$$

where n is the number of atoms per unit of volume. We obtain $\Theta = 82$°K.

The values of V_l and Θ we obtained were very near those for Ag_4RbI_5. Nagoa and Kaneda[11] found that V_l in the [100] direction is 1700 m/sec at room temperature, and the Θ calculated from the elastic constants, was found to be 92°K[12] for this material.

As mentioned in the Introduction, the elastic constants[12] of $RbAg_4I_5$ are discontinuous at the class-II transition at -65°C. They are lower in the low-temperature phase by 4% for C_{44}, by 1% for C_{11}, and by 3% for C_{12}. The most striking difference with our results are the variation of C_{44} at the transition and the absence of a maximum in V_l above the transition temperature.

B. Dielectric losses

Below the transition temperature T_c, the curve $\tan\delta$ as a function of the frequency is only slightly dependent on the type of the electrodes: silver electrodes or blocking electrodes. However, above T_c, the measurements were possible only

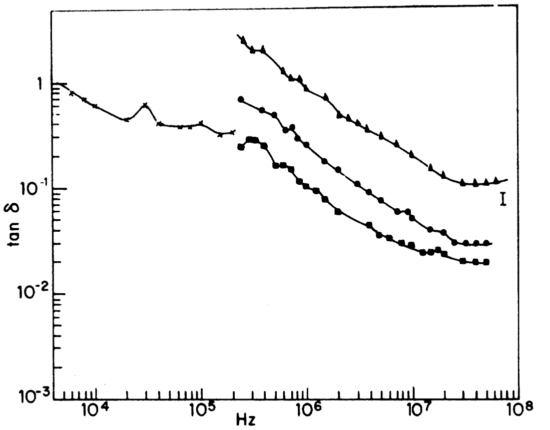

FIG. 2. Variation of tanδ with frequency of $T < T_c$ ($T_c = 51\,°C$) ■ room temperature, blocking electrodes. ● room temperature, silver electrodes. ▲ 47 °C, blocking electrodes, × room temperature, from Ref. 11.

with blocking electrodes, because the samples with silver electrodes have a large ionic conductivity besides their electronic conductivity. The nonblocking electrodes were made with full-strength silver-paint electrodes (Dupont preparation 847). Highly diluted silver paint was found to act as a blocking electrode. This point was verified by measuring the dc conductivity of samples with diluted paint electrodes as a function of T; no sharp discontinuity was found at T_c (see also Ref. 2). The point was further verified by going over the room-temperature measurements with Aquadag-painted electrodes and the same results as with the diluted-Ag painted electrodes were obtained.

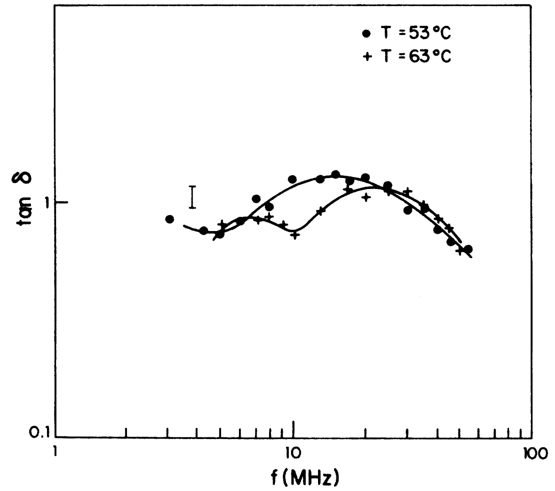

FIG. 3. Variation of tanδ with frequency for $T > T_c$. Note the relaxation peaks.

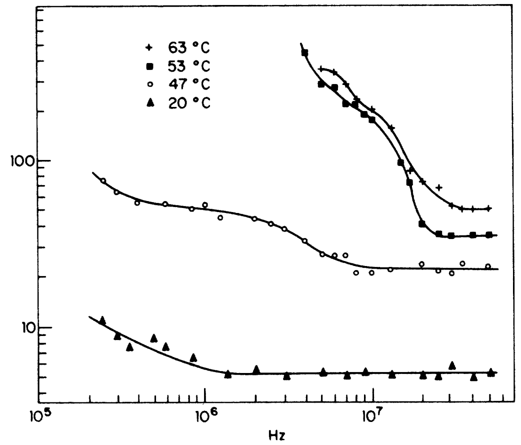

FIG. 4. Variation of the dielectric constant with the frequency at different temperatures.

In Figs. 2 and 3, we present the curves tanδ(ω) at different temperatures. Below T_c, tanδ decreases when ω increases, starting from the maximum at about 0.3 MHz. The curves exhibit local maxima which may be due to relaxations from impurities. In Ref. 13, tanδ was measured at room temperature up to 0.2 MHz and the values obtained are in prolongation of our results. On the other hand, the value of ϵ we measured at 0.25 MHz is twice their value at 0.2 MHz. This discrepancy is perhaps due to the fact that we used painted contacts while Olsen and Harris used pressure contacts.

Above T_c, measurements were possible only down to 3–4 MHz because the loss tangent became too high. The important feature is the appearance of two relaxations. This can be seen very well in the two maxima of the curve tanδ at 63°C and on the curves of the dielectric constant (Fig. 4) at 53 and 63°C, which show two inflection points. From the curve $\epsilon(\omega)$ at 53°C, one can estimate that the second peak in the tanδ curve should appear at 3 MHz. However we were not able to detect it since we were limited in frequency. Above T_c, the values of ϵ are particularly high and this is a consequence of the ionic nature of the charge carriers in this phase. At $T = 47°C$, ϵ also exhibits an inflection point characteristic of a relaxation. This is not visible on the tanδ curve because of the high electronic conductivity background.[2]

IV. DISCUSSION

A. Elastic behavior

In order to discuss the elastic behavior, we shall use the Landau-Devonshire theory of the phase transition.[17] This theory is classical and does not take into account correctly the fluctuations. However, in the case of a linear coupling of the order parameter with the deformation, it is possible to show[18] that this theory is correct. We shall assume that effectively we have a linear coupling between the order parameter and the volume change $\delta = -\Delta V/V$. As shown below, the variation of V_t we observe, or of the bulk modulus B', above T_c is a direct consequence of the linear coupling.

The free energy per unit volume, or more correctly, the contribution to the free energy due to the phase change is expanded as a function of the order parameter η and of the volume change δ (the high-temperature phase is taken as a reference). The order parameter is related to the proportion of Ag ions which are in the "wrong" position, in analogy with the ordered alloys such as CuAu. η is zero above T_c and is different from zero below this temperature. G is written as[18]

$$G = a\eta^2 + b\eta^3 + c\eta^4 + \tfrac{1}{2}B\delta^2 + g\delta\eta - \delta p. \qquad (1)$$

In (1) p is the pressure and B the bulk modulus. Well below T_c the function $a\eta^2 + b\eta^3 + c\eta^4$ has a minimum stable only for $\eta \neq 0$ and well above T_c, the only minimum stable is for $\eta = 0$. To achieve this, it is necessary for the coefficient a to change its sign at the temperature $T_0 < T_c$ (first-order transition) and it is generally assumed that a is linear with T. We shall also make this assumption $a = a_0(T - T_0)$.

We have not included the shear deformation and its coupling with η, since our data shows that V_t does not exhibit a noticeable anomaly at T_c.

We note that (1) does not include the other degrees of freedom of the crystal. In particular, the theory does not include the thermal expansion not related to the phase change. This remark is important when the theoretical predictions are compared with the experimental results.

Finally we note the following convention: p is positive for a compressive force and consequently δ is positive when the volume decreases. δ is given by

$$\frac{\partial G}{\partial \delta} = 0,$$

which makes

$$p = B\delta + g\eta.$$

When $p = 0$, the "spontaneous" δ is equal to

$$\delta = -g\eta/B. \qquad (2)$$

Since experimentally $\delta > 0$ when the sample passes from the disordered to the ordered phase (cf. Fig. 6 of Ref. 2), we have $g < 0$.

Furthermore, we have $\partial G/\partial\eta = 0$, or

$$2a\eta + 3b\eta^2 + 4c\eta^3 + g\delta = 0. \qquad (3)$$

With the help of (2) and (3), one can calculate the values $\eta_0(T)$ and $\delta_0(T)$ which minimize the free energy (1).

To calculate the bulk modulus, we have to differentiate twice the free energy $G_\delta(\eta(\delta), \delta)$ and we get

$$B' = \frac{\partial^2 G_\delta}{\partial \delta^2} = B - \left(\frac{g^2}{2a + 6b\eta + 12\eta^2}\right)_{\eta_0}. \qquad (4)$$

In order to determine the sign of the denominator in (4) we observe that $\partial^2 G_\eta/\partial\eta^2$ is always >0 to insure the stability of the system $[G_\eta = G(\eta, \delta(\eta))]$. We have

$$\frac{\partial^2}{\partial\eta^2} G(\eta, \delta(\eta)) = 2a + 6b\eta + 12c\eta^2 - \frac{2g^2}{B} > 0. \qquad (5)$$

This implies that $2a + 6b\eta + 12c\eta^2$ is also a positive quantity. In other words, $B' - B$ is always negative.

From the expression (4), we draw the following conclusions regarding the behavior of B'. Above T_c, $\eta \equiv 0$ and (4) becomes

$$B' = B - g^2/2a_0(T - T_0). \qquad (6)$$

At the transition temperature T_c (from below) one has

$$G = a_c\eta_c^2 + b\eta_c^3 + c\eta_c^4 + \tfrac{1}{2}B\delta_c^2 + g\delta_c\eta_c = 0.$$

η_c and δ_c are given by (2) and (3), where a is equal to $a_c = a_0(T_c - T_0)$. From that, it is easy to show that $6bn_c + 12\eta_c^2 = 0$ (by the way, this shows that $b < 0$). From (4) and (6), we conclude that B' is continuous at the transition, and consequently V_l is also continuous at T_c. The experimental results of V_l are consistent with a small discontinuity or with a continuity at the transition temperature (Fig. 1).

In order to compare the experimental results with the expression (6), we have to know the variation of B with T. This dependence is not known. We therefore assume that for $T > 70$°C, $B' \simeq B$ as suggested by the behavior of V_l in Fig. 1 and that for $51 < T < 70$°C, the sound velocity of the longitudinal waves, if there were no phase change, would be a linear decreasing function of T as indicated in Fig. 1. This means that we assume that $\sqrt{B}$ decreases linearly when T increases. In Fig. 5, we have drawn $(B - B')^{-1}$ as a function of T (in arbitrary units), and we get a straight line, with $T_0 = 48$°C. Thus we conclude that the assumption of a linear coupling is supported by the experimental results. And this justifies the use of the Landau theory.

The calculation presented above deals with the isothermal value of the bulk modulus, but the

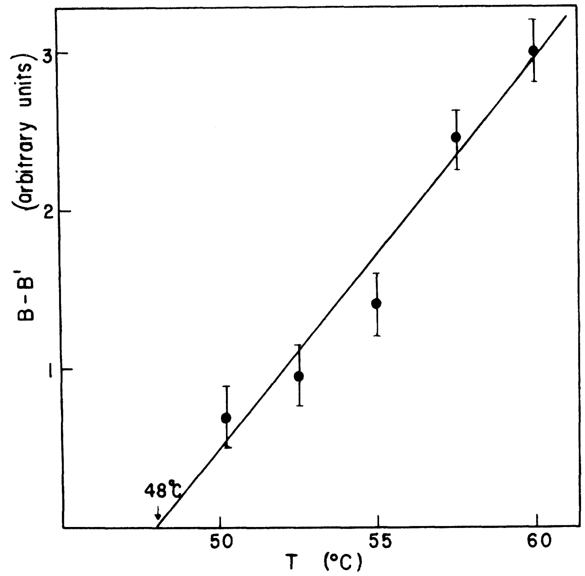

FIG. 5. $(B-B')^{-1}$ as a function of T.

measured value corresponds to the adiabatic situation because of the high frequency (10 MHz) used to measure the sound velocity. However, we have verified, using the formula[9] $B^S - B^T = T\alpha^2 B^2/C$ (α thermal-expansion coefficient, C specific heat), that the difference is negligible, of the order of $10^{-2}B$.

The preceding discussion is based on macroscopic considerations. Huberman and Martin[19] have recently discussed microscopic interactions between the mobile ions (analogous to a fluid) and the ions (rigid lattice). They distinguish between the charged liquid fluctuations and the fluctuations in the local site population. This last type was called pseudospin. All these fluctuations are coupled to the phonons. From their numerical estimation, the largest coupling of the phonons is that with the pseudospin fluctuations. Their pseudospin parameter s is clearly related to our order parameter η. The pseudospin fluctuations can be divided into two types: fluctuations where the ions are redistributed among energetically inequivalent sites and which couple with the volume strain and fluctuations where ions are redistributed among energetically equivalent sites and which couple to the shear strain.

Following their analysis, the absence of anomaly in the transverse waves in our measurements would indicate that the pseudospin fluctuations are those of the first type: redistribution of the mobile ions among energetically inequivalent sites. There are two possible sites[6] for the mobile Ag^+ ions: at the corner or at the face of the cubic cell, and it is natural to expect different energies for the ions in different sites. Thus we can conclude that the fluctuations take place only by the first mechanism, by redistribution between inequivalent sites.

B. Dielectric losses

The relaxations we observed are in agreement with the conclusion of Browall and Kasper,[4] on the thermal-activated motion of Ag^+ ions. We attribute therefore the relaxation peaks we found to the mobile Ag^+ ions. It is interesting to calculate the frequencies of the relaxations. We shall make the same hypothesis as in Ref. 4, i.e., that all the Ag^+ ions participate in the conductivity. Then the mobility can be calculated. We use the results of Ref. 2 for the conductivity since they were also made on polycrystalline samples. At 63°C, we get $\mu = 2.03 \times 10^{-6}$ cm^2/V sec.

The relaxation time is given by[20] $\tau_0 = a^2/nD$, where D is the diffusion coefficient and a the lattice constant and n is the number of the neighboring sites for the ions. Since Ag^+ can be[6] at the corner (12 nearest neighbors) or on the face of the cubic cell (four nearest neighbors), we expect two relaxation frequencies with their ratio equal to 3. The relaxation frequency is $f = (2\pi\tau_0)^{-1}$ or

$$f = nD/2\pi a^2 = n\mu kT/2\pi a^2 e$$

(k is the Boltzmann constant and e the charge of the electron). Taking $a = 6.36$ Å (Ref. 2) and the value of μ quoted above, we get $f_1 = 9$ MHz and $f_2 = 27.6$ MHz. In order to compare with the experiment, we have to determine the relaxation frequencies from the peaks in a $\epsilon'' = \epsilon' \tan\delta$ vs ω plot. We obtained $f_1 \simeq 6$ MHz and $f_2 \simeq 21$ MHz, at 63°C. The agreement is fairly good and gives support to the hypothesis that all the Ag ions participate in the conduction. The increase of f_2 with T is also in agreement with a thermally activated motion.

Below T_c, we found only one relaxation. This could be explained by the release of Ag^+ ions from only one kind of site, but this interpretation is only tentative.

We can compare the results concerning Ag_2HgI_4 with those concerning $RbAg_4I_5$, which have been well studied. In this latter compound the mobility is high,[14] $\mu = 0.05$ cm^2/V sec at room temperature. The ac conductivity has been measured[21] up to 10^8 MHz, at room temperature in the high-conductivity phase. The resistivity decreases with the frequency, with no peak, and above 10^6 Hz the sample is inductive. All these features are interpreted assuming that the ions are, at least partially,[20] free to move in the lattice. The use of the polaron theory[14] implies that in their motion the Ag^+ ions interact with the cations. This picture is very different from that of Browall and Kasper for Ag_2HgI_4 in which the Ag^+ ions are well located in their sites, jump from site to site in crossing the potential barrier and spend most of their time at their sites. This interpretation is supported by the low value of the mobility and the presence of dielectric relaxations like in other, regular, ionic conductors. The relatively large value of the conductivity comes from the large number of ions available for the conductivity.

V. CONCLUSIONS

We have measured the sound velocities in polycrystalline Ag_2HgI_4 and have found that V_l has a marked anomaly at the transition temperature and that V_t very likely does not. The anomaly in the high-temperature phase can be explained assuming that the interaction of the order parameter η and the volume change δ is linear in η and in δ. Thus our results confirm the theoretical predictions of Rehwald.[9] We note that this type of interaction characterizes NH_4Cl,[9] which also exhibits an order-disorder transition.

We have found relaxations in the dielectric losses and this gives support to the picture of a thermally activated motion of the Ag^+ ions. This agrees with the observation of Browall and Kasper[4] and is in contrast with the polaron model which was applied to $RbAg_4I_5$.[10] Finally, we can remark that the conclusion drawn from the sound-velocity measurements, following the microscopic model of Huberman and Martin, is in agreement with our dielectric measurement. In both cases, our data are consistent with random motion of the Ag^+ ions taking place between nearest-neighboring sites which are energetically different sites.

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[1] J. A. A. Ketelaar, Z. Kristallogr. 80, 190 (1931).
[2] R. Weil and A. W. Lawson, J. Chem. Phys. 41, 832 (1974).
[3] W. van Gool, Ann. Rev. Mater. Sci. 4, 311 (1974).
[4] K. W. Browall and J. S. Kasper, J. Solid State Chem. 15, 54 (1975).
[5] A. W. Webb, J. Phys. Chem. Solids 34, 301 (1973).
[6] K. W. Browall, J. S. Kasper, and H. Wiedemeir, J. Solid State Chem. 10, 20 (1974); J. S. Kasper and K. Browall, *ibid*. 13, 119 (1975).
[7] J. A. A. Ketelaar, Z. Phys. Chem. 30B, 53 (1935).
[8] C. W. Garland, in *Physical Acoustics, Principles and Methods*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. 7, p. 53.
[9] W. Rehwald, Adv. Phys. 22, 721 (1973).
[10] W. J. Pardee and G. D. Mahan, J. Solid State Chem. 13, 310 (1975).
[11] M. Nagao and T. Kaneda, Phys. Rev. B 11, 2711 (1975).
[12] L. J. Graham and R. Chang, J. Appl. Phys. 46, 2433 (1975).
[13] C. E. Olsen and P. M. Harris, U.S. Department of Commerce Report No. PB156106 (1959) (unpublished).
[14] T. Kaneda and E. Mizuki, Phys. Rev. Lett. 29, 937 (1972).
[15] D. I. Bolef and M. Menes, J. Appl. Phys. 31, 1010 (1960).
[16] G. A. Alers, in *Physical Acoustics, Principles and Methods*, edited by W. P. Mason (Academic, New York, 1965), Vol. 3B, p. 29.
[17] J. C. Slonczewski and H. Thomas, Phys. Rev. B 1, 3539 (1970).
[18] R. A. Cowley, Phys. Rev. B 13, 4877 (1976).
[19] B. A. Huberman and R. M. Martin, Phys. Rev. B 13, 1498 (1976).
[20] B. A. Huberman and P. N. Sen, Phys. Rev. Lett. 33, 1379 (1974).
[21] R. D. Amstrong and D. Taylor, J. Electronanal. Chem. 63, 9 (1975).