

than the rise of the Fermi level above the conduction band. This may be as much as a 15% change in the band gap (for the most heavily doped specimen studied). This agrees qualitatively with many of the observations previously reported on degenerate germanium^{10,20}: reduced barrier height for hole injection into degenerate *n*-type germanium, reduced energy in reflectivity data for *L*-type transitions¹¹ (here there is also quantitative agreement), reduced barrier height in capacitance measurement,²¹ shift of the emission spectrum to lower energy. However the present work does not explain all of the observations made during emission experiments. For example the presence of two emission mechanisms at different energies, both lower than the gap of pure germanium, does not show a counterpart in the absorption measurement. Although this appears as a lack of

concordance between the two sets of experiments, it is not necessarily an inconsistency since the two methods may not be equally sensitive in revealing the same details of the band structure.

Sommers²² has made another interpretation of various measurements on degenerate germanium with the conclusion that the energy gap is only 30×10^{-3} eV less than in the unperturbed lattice. Since the present measurements lead to quite a different conclusion, the problem of interpreting the various measurements on degenerate germanium is again an open question.

Another conclusion is that the dominant electron scattering mechanism is not a phonon scattering process but rather one dependent on the electron concentration.

ACKNOWLEDGMENT

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²² H. S. Sommers, *Phys. Rev.* **124**, 1101 (1961).

²⁰ D. Meyerhofer, G. A. Brown, and H. S. Sommers (to be published).

²¹ A. G. Chynoweth, W. L. Feldman, C. A. Lee, R. A. Logan, G. L. Pearson, and P. Aigrain, *Phys. Rev.* **118**, 425 (1960).

Field Dependence of the Electric Susceptibility of Ionic Crystals

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An attempt has been made to estimate the field dependence of the electric susceptibility of simple ionic crystals by considering a linear chain of alternating positive and negative ions interacting only through nearest neighbors. The pressure and temperature dependence have also been included to compare with experiment and thereby to give some indication of the reliability of the model. It is found that the dependence on all three parameters is directly related to the anharmonicity in the vibrational motion.

1. INTRODUCTION

FOR the explanation of many properties of crystals it is often sufficient to expand the potential energy as a Taylor series in the displacements of the lattice particles about their equilibrium positions, and to retain only the terms involving the second derivatives. With this "harmonic" approximation one may show in particular that under electric fields, the polarization of a simple ionic crystal is proportional to the field. This relation in turn may be regarded as a first-order Taylor expansion in the field, so that for intense fields one would expect a dependence of the polarization on the cube of the field. This additional dependence would correspond to the inclusion of higher derivatives (the "anharmonic" terms) in the expansion of the potential energy.

In this paper, we attempt to estimate this field dependence for ionic crystals by deriving an expression for the electric susceptibility of a linear chain of alter-

nating positive and negative point ions interacting only with nearest neighbors, and then assuming, after suitable adjustment of dimensions, that this expression actually holds for the 3-dimensional crystal. The problem of field dependence has been treated in general by O'Dwyer¹ but the calculation below gives an expression in terms of constants related directly to the anharmonicity.

Unfortunately there are no data with which to compare the result. However, in the derivation, the temperature and pressure dependence are included also. An order of magnitude calculation for these, in the case of NaCl, then gives figures which agree roughly with values by Bretscher² and Mayburg.³ This gives some indication of the reliability of the model for estimating the order of magnitude for field dependence.

¹ J. J. O'Dwyer, *Proc. Phys. Soc. (London)* **A64**, 1125 (1951).

² E. Bretscher, *Trans. Faraday Soc.* **30**, 684 (1934).

³ S. Mayburg, *Phys. Rev.* **79**, 375 (1950).

2. CALCULATIONS

Following a similar model by Dugdale and MacDonald⁴ and MacDonald and Roy,⁵ we consider a chain of $(N+1)$ ions whose separation at 0°K under zero external field and pressure is a_0 . We suppose the ions carry charges $e, -e$ and have masses m_+, m_- , respectively. The interaction between a positive and a negative ion with separation r is taken as $\phi(r)$, so that with the notation in Fig. 1, the total self-energy of the chain with nearest-neighbor interaction is

$$U_s = \sum_{n=1}^N \phi(a_0 + y_n - y_{n-1}). \quad (1)$$

In the presence of an external field E parallel to the chain, there will be an additional term

$$U_e = \frac{1}{2}eE a_0(n+1) + eE \sum_{n=1,3,5,\dots} (y_n - y_{n-1}), \quad (2)$$

in the energy of the system, the zero of electric potential being taken at the point O (Fig. 1).

We shall assume the first ion of the left (Fig. 1) is fixed. Since, however, the chain has an electric moment to start with, to obtain a more realistic model, the average of two oppositely polarized chains will be taken. This procedure also has the effect of giving an expression containing only even powers of E .

Contrary to the usual case in statistical mechanics, the system here is allowed to expand. The thermodynamic function appropriate to the problem is then

$$G = U - TS + PL - E\mathcal{P}, \quad (3)$$

where U, T, S have the usual meanings, P is the (compressive) force at the ends of the chain, E is the external field, and L and \mathcal{P} are the length and total polarization of the chain, respectively. Brown⁶ has shown that the corresponding classical partition function is

$$Z = \exp(-G/kT) = \int \int \exp[-(H + PL)/kT] dp dq, \quad (4)$$

where

$$H = \sum_{n=1}^N \frac{p_n^2}{2m_n} + U_s + U_e$$

and

$$L = Na_0 + \sum_{n=1}^N (y_n - y_{n-1}).$$

On setting $x_n = y_n - y_{n-1}$, and neglecting ± 1 with respect to N , we get

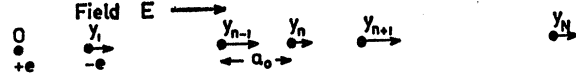


FIG. 1. Instantaneous displacements at T (°K) under a field E and a (compressive) force P , measured from the equilibrium position at 0°K under zero field and zero force.

$$\begin{aligned} Z &= \{ \exp[-Na_0(P + \frac{1}{2}eE)/kT] \} (2\pi kT)^{N/2} (m_+ m_-)^{N/4} \\ &\times \int_{-a_0}^{\infty} dy_1 \int_{-a_0+y_1}^{\infty} dy_2 \cdots \int_{-a_0+y_{N-1}}^{\infty} dy_N \\ &\times \exp\left\{ - \sum_{n=2,4,\dots} [\phi(a_0 + x_n) + Px_n]/kT \right. \\ &\quad \left. - \sum_{n=1,3,5,\dots} [\phi(a_0 + x_n) + (P + eE)x_n]/kT \right\} \\ &= \{ \exp[-Na_0(P + \frac{1}{2}eE - D/a_0)/kT] \} (2\pi kT)^{N/2} \\ &\quad \times (m_+ m_-)^{N/4} [J(P)]^{N/2} [J(P + eE)]^{N/2}, \quad (6) \end{aligned}$$

where

$$D = -\phi(a_0)$$

and

$$J(P) = \int_{-a_0}^{\infty} \exp\{ -[\phi(a_0 + x) + D + Px]/kT \} dx. \quad (7)$$

Thus by (3), (4), and (6), the susceptibility of the chain is

$$\begin{aligned} \chi_{P,T} &= L^{-1}(\partial \mathcal{P} / \partial E)_{P,T} = -L^{-1}(\partial^2 G / \partial E^2)_{P,T} \\ &= \frac{e^2 N k T}{2L} \frac{\partial^2 \ln J(\xi)}{\partial \xi^2} \bigg|_{\xi=P+eE}. \quad (8) \end{aligned}$$

Another quantity whose temperature and pressure variation depend on anharmonicity is the isothermal compressibility $K_T(P)$. Again by (3), (4), and (6) we have

$$\begin{aligned} K_T(P) &= -L^{-1}(\partial L / \partial P)_{T,E=0} = -L^{-1}(\partial^2 G / \partial P^2)_{T,E=0} \\ &= \frac{N k T}{L} \frac{\partial^2 \ln J(P)}{\partial P^2}. \quad (9) \end{aligned}$$

It follows, therefore that the susceptibility may be expressed in the form

$$\chi_{P,T} = (e^2/2) [K_T(P) + (e^2 E^2/2) K_T''(P) + \cdots], \quad (10)$$

where the primes denote differentiation with respect to pressure.

If we neglect the field dependence, we can translate this expression to three dimensions by assuming the crystal built up of unit chains each of which contributes $\chi_{P,T} = e^2 K_T/2$ to the total susceptibility. Thus, a unit cube with nearest-neighbor distance a_0 will contain $1/a_0^3$ chains, giving a susceptibility of $\chi_{P,T}/a_0^3 = e^2/(2a_0^3)(\partial L/\partial P)_{L=1}$. Now since P is the force at the ends

⁴ J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **96**, 57 (1954).

⁵ D. K. C. MacDonald and S. K. Roy, Phys. Rev. **97**, 673 (1955).

⁶ W. B. Brown, Molecular Phys. **1**, 65 (1958).

of the chain, the pressure on the cube is P/a_0^2 and hence the compressibility

$$\beta = [L^{-3} \partial L^3 / \partial (P/a_0^2)]_{L=1} = 3a_0^2 (\partial L / \partial P)_{L=1}.$$

The susceptibility of the cube is therefore $e^2 \beta / (6a_0^4)$. For NaCl we have $a_0 = 2.81 \times 10^{-8}$ cm and $\beta = 4.26 \times 10^{-12}$ cm² dyne⁻¹,⁷ giving a susceptibility of 0.27 esu/cm³. In view of the assumptions made this compares favorably with the observed value 0.27 esu/cm³ obtained from the static dielectric constant $\epsilon_s = 5.62$ and the optical dielectric constant $\epsilon_0 = 2.25$. Similarly for KCl, the values are⁷ $a_0 = 3.14 \times 10^{-8}$ cm and $\beta = 5.63 \times 10^{-12}$ cm² dyne⁻¹, giving a susceptibility of 0.22 esu/cm³. The observed value is 0.20 esu/cm³.

We note also that (10) allows us to relate the pressure and temperature dependence of the susceptibility to those of the compressibility:

$$\chi_{P,T}^{-1} (\partial \chi_{P,T} / \partial T) = K_T^{-1} (\partial K_T / \partial T), \quad (11)$$

and

$$\chi_{P,T}^{-1} (\partial \chi_{P,T} / \partial P) = K_T^{-1} (\partial K_T / \partial P). \quad (12)$$

These relations may carry over, as they stand, to three dimensions, P now being interpreted as the pressure, and $K_T, \chi_{P,T}$ as the (isothermal) compressibility and susceptibility of the solid, respectively.

Evaluation of the Integral $J(P)$

On substituting $y = (a/kT)^{1/2} x$ in (8), where $a = \phi''(a_0)/2$, and expanding $\phi(a_0 + x)$ about the equilibrium position a_0 , we get

$$J(P) = (kT/a)^{1/2} \int_{-a_0(a/kT)^{1/2}}^{\infty} \exp \left\{ -y^2 - \left[\frac{b}{a} \left(\frac{kT}{a} \right)^{1/2} y^3 + \frac{c}{a} \left(\frac{kT}{a} \right) y^4 + \dots \right] - \frac{Py}{(akT)^{1/2}} \right\} dy, \quad (13)$$

where $b = \phi'''(a_0)/3!$, $c = \phi''''(a_0)/4!$, etc.

Now $\phi''(a_0) \approx c_{11}a_0$,⁸ where c_{11} is the elastic constant. Thus in the case of NaCl, $a \approx 0.69 \times 10^4$ dyne cm⁻¹. Hence at 300°K, $(a/kT)^{1/2} \approx 4.1 \times 10^{+8}$ cm⁻¹. Corresponding to a pressure of one atm, the equivalent compressive force $P \approx 10^6 \times (\text{lattice distance})^2 = 7.9 \times 10^{-10}$ dyne, and $P/(akT)^{1/2} \approx 4.7 \times 10^{-5}$. Since in effect the motion of the ions is confined to a space $< 10^{-8}$ cm about their equilibrium positions, the contribution to $J(P)$ from outside this range must be negligible. Hence we may expand $\exp[-Py/(akT)^{1/2}]$ and

$$\exp \left\{ - \left[(b/a)(kT/a)^{1/2} y^3 + (c/a)(kT/a) y^4 + \dots \right] \right\}$$

separately and retain only a few terms, and then re-

place the lower limit by $-\infty$. Thus

$$J(P) = \left(\frac{kT}{a} \right)^{1/2} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left[\frac{P}{(akT)^{1/2}} \right]^n \times \int_{-\infty}^{+\infty} \exp(-y^2) y^n \left\{ 1 - \left[\frac{b}{a} \left(\frac{kT}{a} \right)^{1/2} y^3 + \frac{c}{a} \left(\frac{kT}{a} \right) y^4 \right] - \frac{1}{2} \left[\frac{b^2}{a^2} \left(\frac{kT}{a} \right) y^6 + \frac{2bc}{a^2} \left(\frac{kT}{a} \right)^{3/2} y^7 + \frac{c^2}{a^2} \left(\frac{kT}{a} \right)^2 y^8 \right] \right\} dy \\ \equiv (\pi kT/a)^{1/2} (1+F), \text{ say.} \quad (14)$$

In evaluating F we retain terms up to order $(b/a)^2$, supposing c/b to be of the same order as b/a .⁹ We then obtain

$$F = \frac{3kT}{4a} \left(\frac{5b^2}{4a^2} - \frac{c}{a} \right) + \frac{3b}{4a} \left(\frac{kT}{a} \right)^{1/2} \frac{P}{(akT)^{1/2}} + \left[1 + \frac{15kT}{4a} \left(\frac{7b^2}{4a^2} - \frac{c}{a} \right) \right] \frac{P^2}{4akT} + \frac{5b}{16a} \left(\frac{kT}{a} \right)^{1/2} \frac{P^3}{(akT)^{3/2}} + \left[1 + \frac{35kT}{4a} \left(\frac{9b^2}{4a^2} - \frac{c}{a} \right) \right] \frac{P^4}{32(akT)^2}. \quad (15)$$

The Susceptibility

Since $F \ll 1$, we may expand $\ln(1+F)$ and rearrange as a power series in $P/(akT)^{1/2}$

$$\ln(1+F) \approx c_0 + c_1 \frac{P}{(akT)^{1/2}} + \dots + c_4 \frac{P^4}{(akT)^2}, \quad (16)$$

where

$$c_2 = \frac{1}{4} \left[1 + \frac{3kT}{a} \left(\frac{3b^2}{2a^2} - \frac{c}{a} \right) \right], \quad c_3 = \frac{7b}{32a} \left(\frac{kT}{a} \right)^{1/2},$$

$$c_4 = \frac{kT}{16a} \left(\frac{9b^2}{4a^2} - \frac{c}{a} \right);$$

c_0 and c_1 are not required. From (9), (14), and (16) we then have

$$K_T(P) = \frac{N}{aL} \left[\frac{1}{2} + \left(\frac{3b^2}{2a^2} - \frac{c}{a} \right) \frac{3kT}{2a} + \frac{3bP}{16a^2} + \left(\frac{9b^2}{4a^2} - \frac{c}{a} \right) \frac{3P^2}{4a^2} \right], \quad (17)$$

and finally, for the susceptibility of the chain,

$$\chi_{P,T} = \frac{e^2}{4aa_0} \left[1 + \left(\frac{3b^2}{2a^2} - \frac{c}{a} \right) \frac{3kT}{a} + \frac{3bP}{8a^2} + \left(\frac{9b^2}{4a^2} - \frac{c}{a} \right) \frac{3e^2 E^2}{2a^2} \right], \quad (18)$$

where we have put $L \approx Na_0$.

⁷ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 26.

⁸ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 113.

⁹ R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 35.

TABLE I. Experimental data for NaCl used in calculating the parameters of the theory. c_{11} is from reference 8, page 93, and a_0 and α from reference 3. $K_T^{-1}(\partial K_T/\partial T)$ was deduced from reference 10.

c_{11} (dyne cm ⁻²)	a_0 (cm ⁻¹)	α (°K) ⁻¹	$K_T^{-1}(\partial K_T/\partial T)$ (°K) ⁻¹	a (cm ⁻²)	b/a (cm ⁻¹)	$3b^2/(2a^2) - c/a$ (cm ⁻²)
4.9×10^{11}	2.81×10^{-8}	4.0×10^{-5}	5.5×10^{-4}	6.9×10^3	-7.5×10^7	9.2×10^{15}

The Anharmonic Contribution

In spite of the simplicity of the model treated here, the main features of (18) should persist in three dimensions. We therefore assume, in order to estimate the temperature, pressure, and field dependence for NaCl, that (18), after suitable adjustment of dimensions, actually holds for the 3-dimensional crystal. We shall also assume the same for (17) to be able to eliminate the unknown parameter c/a .

Thus if χ now denotes the susceptibility per unit volume and P the pressure, we have

$$\chi^{-1} \partial \chi / \partial T \approx 3k[3b^2/(2a^2) - c/a]/a, \quad (19)$$

$$\chi^{-1} \partial \chi / \partial P \approx 3a_0^2 b / (8a^2) \quad (20)$$

$$\chi^{-1} \partial \chi / \partial (E^2) \approx 3e^2[9b^2/(4a^2) - c/a]/a^2. \quad (21)$$

(19) and (21) follow immediately from (18). In (20) however, a factor a_0^2 arises from the conversion of P from a force in (18) to a pressure in (20).

The quantities (19)–(21) will now be evaluated for NaCl. The right-hand side of (19) is immediately obtained by using the variation of the isothermal compressibility with temperature,

$$K_T^{-1} \partial K_T / \partial T \approx 3k[3b^2/(2a^2) - c/a]/a. \quad (22)$$

This latter quantity was deduced from measurements by Durand¹⁰ of the isothermal elastic constants of NaCl. We may then dispose of c/a in (21) by replacing $[3b^2/(2a^2) - c/a]$ by $aK_T^{-1}(\partial K_T/\partial T)/(3k)$. Next, a may be obtained as before from the elastic constant c_{11} : $a = \phi''(a_0)/2 \approx c_{11}a_0/2$. Lastly b/a may be obtained from the coefficient of linear thermal expansion α which, on the same model, is given by⁵

$$\alpha = 3kb/(4a^2a_0).$$

TABLE II. Comparison of the experimental and theoretical results for the temperature and pressure variation of the susceptibility of NaCl. The experimental values were deduced from reference 3.

$\chi^{-1} \partial \chi / \partial T$ (°K ⁻¹)		$\chi^{-1} \partial \chi / \partial P$ (cm ² dyne ⁻¹)	
(1) Theor.	(2) Exp.	(3) Theor.	(4) Exp.
5.5×10^{-4}	5.7×10^{-4}	-3.2×10^{-12}	-16.3×10^{-12}

¹⁰ M. Durand, Phys. Rev. **50**, 449 (1936).

In Table I are collected the relevant data, together with the values of a , b/a , and $[3b^2/(2a^2) - c/a]$.

In Table II we compare the values of $\chi^{-1}(\partial \chi / \partial T)$ and $\chi^{-1} \partial \chi / \partial P$ obtained from (19) and (20) [Columns (1) and (3)] with values deduced from experimental results in Mayburg³ [Columns (2) and (4)].

Finally we estimate the field dependence of the susceptibility. Using the values from Table I in Eq. (21), we have

$$\chi^{-1} \partial \chi / \partial (E^2) \approx 1.9 \times 10^{-10}, \quad (\text{cgs})$$

or, putting it differently,

$$\Delta \chi / \chi \approx 1.9 \times 10^{-10} \Delta (E^2), \quad (23)$$

for corresponding changes $\Delta \chi$, $\Delta (E^2)$ at constant pressure and temperature. Taking as a sample value a field change of the order of 300 000 volts/cm (1000 esu/cm), we get

$$\Delta \chi / \chi \approx 1.9 \times 10^{-4}; \quad (24)$$

that is, the susceptibility changes by about 0.02%.

Unfortunately there are no data with which to compare this result and we can only point out which of the assumptions made may cause it to be in error. Firstly, there is the extension of the one-dimensional expression to three dimensions; secondly, the fact that only nearest-neighbor interaction was considered; thirdly, that the method of evaluating a , b/a , and $[3b^2/(2a^2) - c/a]$ was uncertain; and fourthly that the electronic contribution to the polarization was neglected. As regards the evaluation of a and b/a , we note that if the values in Table I were used together with (22), to obtain c/a , this quantity would be negative. It appears therefore that a lower value of a or a higher value of b/a should be used. This would tend to bring the estimated value of $\chi^{-1} \partial \chi / \partial P$ more in agreement with the observed value. However, in view of the figures in Table II, it seems unlikely that the first three approximations would seriously affect the estimate (24). The same conclusion also holds for the fourth approximation, since in general the main contribution to the polarization (under static fields) is from the displacements of the ions.

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