

much larger than the unit cell of the crystal.<sup>12-14</sup> At large magnetic fields the dimensions of the wave function perpendicular to the field are reduced, but remain greater than  $0.1a_0^*$  when  $\gamma < 100$ . Thus for semiconductors with low effective mass ( $m^* \sim 0.01m$ ), the approximation can be regarded as representative when the field is less than  $\gamma \sim 100$ .

Demkov and Drukarev<sup>4</sup> have considered particles in a  $\delta$ -function potential and magnetic field. They conclude that for an arbitrarily weak potential which yields no bound state and is characterized by a negative scattering length, an arbitrarily weak magnetic field is sufficient to introduce a bound state. This of course is directly contradictory to our results. Demkov and Drukarev use a procedure in which the  $r \rightarrow 0$  limit of the wave function in the presence of the magnetic field is equated with the zero field form, a procedure which we have not been able to justify. Indeed, if the scattering method of Demkov and Drukarev is applied to a problem which is solvable by other methods (i.e., square-well potential, no mag-

netic field), it does not yield a criterion for the existence of a bound state. This method merely expresses consistency of the sign of the scattering length with the sign of the energy.

The experimental results of Frederikse and Hosler and of Keyes and Sladek are in good agreement with the results of our calculations when  $N_I \sim 10n_c(0)$ , but not  $N_I \sim 400n_c(0)$ . As well as inaccuracy in our calculations (or limitations of the screening length theory), a possible explanation would be that the electric field in this case was sufficiently high to increase the number of free carriers by impact ionization. Experimentally, the applied electric field must be increased at high concentrations of free carriers to maintain Hall voltages comparable to when the concentration is much less.

Although our calculation shows the essential features of the model, clearly an accurate numerical solution of the Schrödinger equation Eq. (2) would be a considerable improvement on the variational calculation. In addition, a more satisfactory comparison of theory with experiment could be made if measurements of the Hall constant were conducted at a temperature of  $\sim 1^\circ\text{K}$ , at fields up to 100 kG or higher, and with a number of impurity concentrations in the range  $n_c(0) < N_I < 10^4 n_c(0)$ .

<sup>12</sup> J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

<sup>13</sup> R. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 196 (1960).

<sup>14</sup> H. Hasegawa and R. E. Howard, J. Phys. Chem. Solids **21**, 179 (1960).

## Lattice Dynamics of Diamond

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The lattice dynamics of diamond has been investigated on the basis of the Cochran version of the dipole-approximation model. Results have been presented for the dispersion curves, and effective calorimetric and x-ray Debye temperatures of diamond. The effective calorimetric and x-ray Debye temperatures of germanium have also been obtained.

### INTRODUCTION

EXPERIMENTAL studies of the inelastic scattering of slow neutrons by crystals have recently made it possible to determine directly the relation between frequency and wave number of the normal modes of a crystal. Germanium was one of the first substances to be investigated by this technique by Brockhouse and Iyengar<sup>1</sup> and by Ghose *et al.*<sup>2</sup>

A detailed analysis of these results by Herman<sup>3</sup> and by Pope<sup>4</sup> showed that to fit all the data concerned it

was necessary to include interactions out to fifth neighbors in the general force model. The theory then involves numerous parameters which have no clear physical significance. Cole and Kineke<sup>5</sup> calculated the vibrational spectrum of Ge using the force constants of Herman.<sup>3</sup>

Lax<sup>6</sup> proposed to fit the data to a force model involving one parameter to represent electrostatic interaction between quadrupoles generated by the lattice vibrations, and as many near-neighbor parameters as proves necessary.

<sup>1</sup> B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

<sup>2</sup> A. Ghose, H. Palevsky, D. J. Hughes, I. Pelah, and C. M. Eisenhauer, Phys. Rev. **113**, 49 (1959).

<sup>3</sup> F. Herman, J. Phys. Chem. Solids **8**, 405 (1959).

<sup>4</sup> N. K. Pope, in *Proceedings of the International Conference on*

*Lattice Dynamics*, Copenhagen (Pergamon Press, Inc., New York, 1964), p. 147.

<sup>5</sup> H. Cole and E. Kineke, Phys. Rev. Letters **1**, 360 (1958).

<sup>6</sup> M. Lax, Phys. Rev. Letters **1**, 133 (1958).

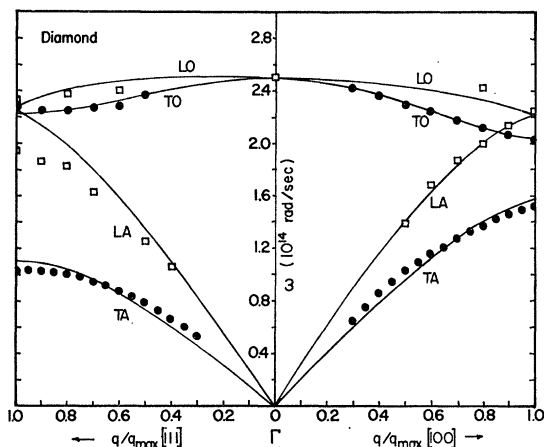


FIG. 1. Dispersion curves of diamond. The experimental points shown by squares and circles are due to Warren, Wenzel, and Yarnell (Ref. 17).

The shell model of an atom has had some success in accounting for the dielectric properties<sup>7,8</sup> and lattice dynamics of alkali-halide crystals.<sup>9</sup>

Cochran<sup>10</sup> applied a simple shell model to germanium. Each atom was regarded as composed of a core of charge  $Z$  coupled to an oppositely charged shell by means of an isotropic spring of constant  $k$ . He assumes three types of nearest-neighbor interactions, the core-core, core-shell and shell-shell interactions. Two force constants specify each type. One is associated with the radial force and the other with the angular force. The formation of dipoles by the lattice wave gives rise to electrostatic forces throughout the crystal. This interaction includes all neighbors and requires no extra parameter. Therefore the shell model involves a total of eight parameters. One of them is shown to be redundant and is eliminated by specifying the polariz-

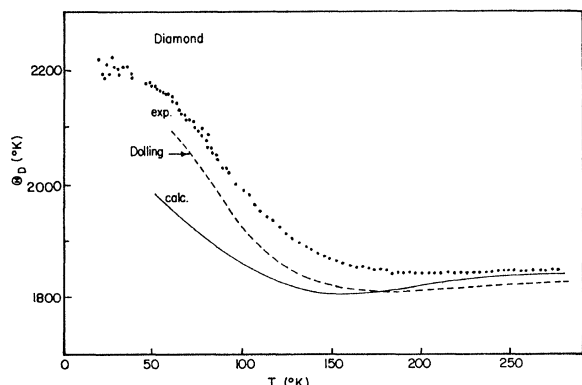


FIG. 2. The calculated and experimental effective calorimetric Debye temperatures for diamond. The experimental points are from Desnoyers and Morrison (Ref. 21).

<sup>7</sup> B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

<sup>8</sup> J. E. Hanlon and A. W. Lawson, Phys. Rev. **113**, 472 (1959).

<sup>9</sup> A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

<sup>10</sup> W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).

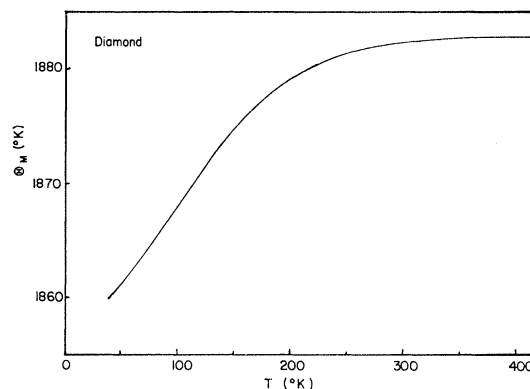


FIG. 3. The calculated effective x-ray Debye temperature as a function of temperature for diamond.

ability  $\beta$  in terms of  $Z$  and  $k$ . Then Cochran reduces the number to five by setting the ratio  $\gamma$  of the angular force constant to the radial force constant equal for the three types of short-range interactions. Under these restrictions the Born identity is satisfied. Two of the remaining five parameters are fixed by fitting them with the elastic-constant data. The polarizability  $\beta$  is then calculated from the experimental value of the dielectric constant. The two remaining parameters are chosen by trial (along with a 5% adjustment in  $\beta$ ) to fit the neutron-scattering data. The agreement is reasonably good except for the longitudinal acoustic mode in the  $[111]$  direction, where, for the point  $q = q_{\max}$  the observed and calculated frequency differ by 14%.

Cochran has also provided some theoretical justification for his work by showing its equivalence to the results of Mashkevich and Tolpygo,<sup>11</sup> who used a quantum mechanical approach. It is now generally recognized that both models are essentially dipole approximation. Cochran also showed that the short-range parameters determine a long-range force.

With the aid of the adiabatic approximation, the potential energy of lattices of the diamond type was found by Mashkevich and Tolpygo<sup>11</sup> in the form of a quadratic form in the displacements and dipole moments of the electronic shells of all atoms. In an extension of

TABLE I. Data for diamond.

Elastic constants <sup>a</sup>	$c_{11} = 10.76 \times 10^{12}$ dyn/cm
	$c_{12} = 1.25 \times 10^{12}$ dyn/cm
	$c_{44} = 5.758 \times 10^{12}$ dyn/cm
Lattice constant <sup>b</sup>	$2r_0 = 3.567 \times 10^{-8}$ cm
Raman frequency <sup>c</sup>	$\omega_R(\Gamma) = 2.509 \times 10^{14}$ rad/sec
Dielectric constant <sup>d</sup>	$\epsilon = 5.66$

<sup>a</sup> H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957).

<sup>b</sup> *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed.

<sup>c</sup> F. A. Johnson and R. Loudon, Proc. Roy. Soc. (London) **A281**, 274 (1964).

<sup>d</sup> D. F. Gibbs and G. J. Hill, Phil. Mag. **9**, 367 (1964).

<sup>11</sup> V. S. Mashkevich and K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. **32**, 520 (1957) [English transl.: Soviet Phys.—JETP **5**, 435 (1957)].

TABLE II. Values of parameters in Cochran's model.

	$R_0$ ( $10^5$ dyn/cm)	$B_1$ ( $10^5$ dyn/cm)	$B_2$	$\beta$	$\gamma_R$	$\gamma_S$	$\gamma_T$
Germanium	2.9233	4.099	3.2	0.105	0.6905	0.6905	0.6905
Diamond	15.5	13.668	0.982	0.094	0.68	0.16	0.96

this work, Tolpygo<sup>12</sup> showed that Cochran's procedure of introducing mixed terms corresponding to the dipole moments of the immediate neighbors into the potential energy is justified. This theory, while formally equivalent to that of Cochran, was based not on a model representation but only on the concept of a weak distortion of electron wave functions due to atomic vibrations. It has nine parameters. Tolpygo's theory was applied to germanium by Demidenko, Kucher, and Tolpygo,<sup>13,14</sup> and to silicon by Kucher.<sup>15</sup>

Recently Warren, Wenzel, and Yarnell<sup>16,17</sup> have measured the dispersion curves for phonons propagating in the [100] and [111] directions

In the present paper we have investigated the lattice dynamics of diamond on the basis of the Cochran version of the dipole-approximation model. Results have been presented for the dispersion curves, and effective calorimetric and x-ray Debye temperatures of diamond. We have also obtained the effective calorimetric and x-ray Debye temperatures of germanium.

While the present work was in progress, a paper by Dolling and Cowley<sup>18</sup> has appeared in which they have applied a dipole-approximation model to diamond, silicon, germanium, and gallium arsenide. This model includes second-nearest-neighbor interactions and has 11 parameters. The work of Dolling and Cowley is more complete than ours. A comparison of our results with those of Dolling and Cowley has been carried out.

## RESULTS

The experimental data used in determining the parameters, besides the dispersion curves, are given in Table I. We have followed the same notation for parameters as that of Cochran<sup>10</sup>; the values of these parameters for diamond as determined here are shown in Table II. Values for germanium as given by Cochran are also shown in the same table. It was found necessary to

<sup>12</sup> K. B. Tolpygo, Fiz. Tverd. Tela 3, 943 (1961) [English transl.: Soviet Phys.—Solid State 3, 685 (1961)].

<sup>13</sup> Z. A. Demidenko, T. I. Kucher, and K. B. Tolpygo, Fiz. Tverd. Tela 3, 2482 (1962) [English transl.: Soviet Phys.—Solid State 3, 1803 (1962)].

<sup>14</sup> Z. A. Demidenko, T. I. Kucher, and K. B. Tolpygo, Fiz. Tverd. Tela 4, 104 (1962) [English transl.: Soviet Phys.—Solid State 4, 73 (1962)].

<sup>15</sup> T. I. Kucher, Fiz. Tverd. Tela 4, 992 (1962) [English transl.: Soviet Phys.—Solid State 4, 729 (1962)].

<sup>16</sup> J. L. Yarnell, J. L. Warren, and R. G. Wenzel, Phys. Rev. Letters 13, 13 (1964).

<sup>17</sup> J. L. Warren, R. G. Wenzel, and J. L. Yarnell, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1965), Vol. 1, p. 361.

<sup>18</sup> G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) 88, 463 (1966).

assume different values of  $\gamma_R$ ,  $\gamma_S$ , and  $\gamma_T$  for diamond in contrast to the case of germanium where they may be taken to be equal.

The calculated dispersion curves of diamond together with the experimental points are shown in Fig. 1. The vibrational frequency distribution  $g(\nu)$  was obtained by calculating the frequencies at 1685 points within the irreducible 48th of the first Brillouin zone; the point  $\mathbf{q} = (0,0,0)$  was left out because of singularity in Coulomb coefficients at this point. These points were weighted, giving a total of 383 994 frequencies and a histogram for  $g(\nu)$  was obtained; its shape was similar to that of Ref. 18. This distribution was used to calculate effective calorimetric ( $\Theta_D$ ) and x-ray ( $\Theta_M$ ) Debye temperatures, which are shown in Figs. 2 and 3, respectively.

Calculations were also carried out for germanium using the parameters given by Cochran; the resulting histogram for the vibration spectrum was in satisfactory accord with that obtained by Fray *et al.*<sup>19</sup> using the same model. Calculated values of  $\Theta_D$  and  $\Theta_M$  are shown in Figs. 4 and 5, respectively.

The results for calorimetric  $\Theta_D$  obtained by Dolling and Cowley<sup>18</sup> are also shown in Figs. 2 and 4.

## DISCUSSION

As far as possible we have attempted to keep the values of the parameters not far from the values ex-

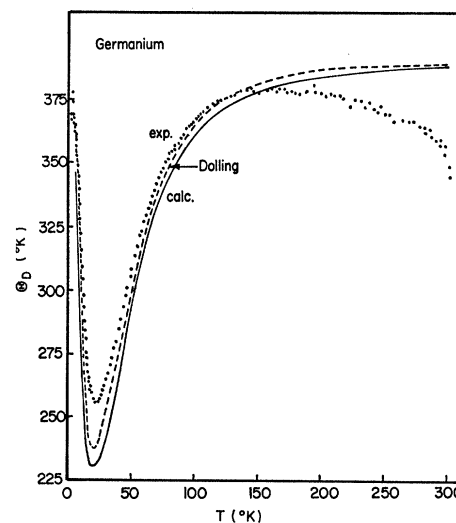


Fig. 4. The calculated and experimental effective calorimetric Debye temperatures for germanium. The experimental points are from Flubacher, Leadbetter, and Morrison (Ref. 24).

<sup>19</sup> S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, Proc. Phys. Soc. (London) 85, 153 (1965).

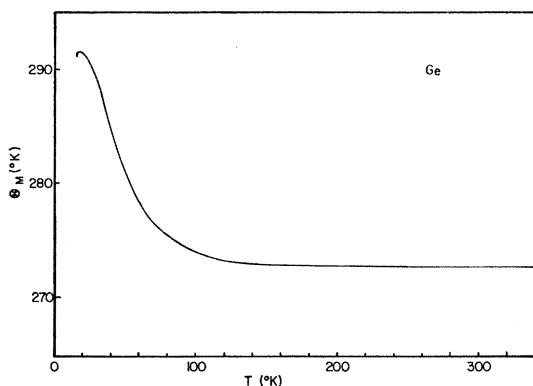


FIG. 5. The calculated effective x-ray Debye temperatures of germanium.

pected for the rigid-ion model and consistent with other physical data.

We quote below the rigid-ion values obtained on the assumption  $\gamma_R = \gamma_T$ :

$$R_0 = 15.295 \times 10^5 \text{ dyn/cm},$$

$$\gamma = 0.682,$$

which may be compared to the corresponding values in Table II. The atomic polarizability can be calculated using the dielectric constant given in Table I. Thus

$$\beta = (3/8\pi)(\epsilon - 1)/(\epsilon + 2) = 0.07.$$

The value adopted here is larger than this value but physically quite reasonable. We may note that the results are rather sensitive to the values of  $\beta$ ,  $\gamma_R$ , and  $\gamma_T$ , but not to the value of  $\gamma_S$ .

The fit of the dispersion curves in the [100] direction is quite satisfactory. The differences between experimental points and theoretical curves being of the same order as the estimated accuracy of the experimental data, given as  $\sim 3\%$  by Warren *et al.*<sup>17</sup>

But in the [111] direction the theoretical LA curve deviates appreciably from the experimental points. We may note that for germanium, with this model, Cochran<sup>10</sup> was also not able to achieve agreement between theory and experiment for this branch. The agreement for the LO branch is also not completely

TABLE III. Measured values of effective x-ray Debye temperature  $\Theta_M$ .

Substance	Measured value of $\Theta_M$ (°K)	Temperature range	Source
Diamond	1491		a
	1549		b
	1990 ± 80		c, d
Germanium	290 ± 5	300° to 1100°K	e
	286 ± 9	300°K	f

<sup>a</sup> S. Göttlicher and E. Wölfel, *Z. Elektrochem.* **63**, 891 (1959), as quoted in Ref. d.

<sup>b</sup> G. P. Carpenter, *J. Chem. Phys.* **32**, 525 (1960), as quoted in Ref. d.

<sup>c</sup> B. Post, *Acta Cryst.* **13**, 1103 (1960), as quoted in Ref. d.

<sup>d</sup> F. H. Herbstein, *Advan. Phys.* **10**, 313 (1961).

<sup>e</sup> B. W. Batterman and D. R. Chipman, *Phys. Rev.* **127**, 690 (1962).

<sup>f</sup> Ya. S. Umanskii and V. I. Prilepskii, *Fiz. Tverd. Tela* **7**, 2958 (1966) [English transl.: *Soviet Phys.—Solid State* **7**, 2399 (1966)].

TABLE IV. Limiting values of  $\Theta_M$  (at fixed volume) calculated from heat capacities by Barron *et al.* (Ref. 23).

	Diamond	Ge
$\Theta_M(0)$	1890°K	311°K
$\Theta_M(\infty)$	1970°K	297°K

satisfactory. It is of interest to note that Kucher and Nechiporuk,<sup>20</sup> even with a nine-parameter model, based on Tolpygo's theory, could not obtain agreement for LO and TO branches in the [111] direction for diamond; indeed their results are less satisfactory than ours.

It is customary to express heat-capacity measurements in terms of the variation of the Debye temperature  $\Theta_D$  as shown in Fig. 2. The experimental points are due to Desnoyers and Morrison.<sup>21</sup> At temperatures greater than 150°K the theoretical curve is in agreement with the experimental data within the combined experimental errors of the thermodynamic and neutron scattering data ( $\sim 3\%$ ). But at low temperatures the theoretical values are too low. The theoretical curve due to Dolling and Cowley also lies below the experimental points.

The available experimental values of  $\Theta_M$  are summarized in Table III. Barron *et al.*<sup>22,23</sup> have shown that, within the quasiharmonic approximation, it is possible to calculate Debye-Waller factors from analyses of appropriate heat-capacity and thermal-expansion data for simple crystals. Limiting values of  $\Theta_M$  thus obtained by them for diamond and germanium are shown in Table IV.

The experimental values of  $\Theta_M$  for diamond are seen to have considerable spread. The theoretical curve (Fig. 3) lies between the experimental values and is not far from the calculated values of Barron *et al.*

The calorimetric Debye temperature curve for germanium (Fig. 4) is seen to fall slightly below the experimental values<sup>24</sup> and is very close to that obtained by Dolling and Cowley.<sup>18</sup> The theoretical  $\Theta_M$  curve (Fig. 5) appears to be on the low side as compared to the experimental values and the calculated values due to Barron *et al.*

#### ACKNOWLEDGMENTS

The authors are thankful to Dr. J. A. Morrison for helpful discussions, and to the National Research Council of Canada for financial support.

<sup>20</sup> T. I. Kucher and V. V. Nechiporuk, *Fiz. Tverd. Tela* **8**, 317 (1966) [English transl.: *Soviet Phys.—Solid State* **8**, 261 (1966)].

<sup>21</sup> J. E. Desnoyers and J. A. Morrison, *Phil Mag.* **3**, 42 (1958).

<sup>22</sup> T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 49.

<sup>23</sup> T. H. K. Barron, M. L. Klein, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 415.

<sup>24</sup> P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *Phil. Mag.* **4**, 273 (1959).