

## Debye Characteristic Temperatures of Certain Noncubic Crystals

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The Debye characteristic temperatures of noncubic crystals with a principal axis of symmetry are evaluated by an expansion of the integrand involved in terms of harmonic polynomials having the same symmetry as the corresponding Christoffel equations of elasticity theory. We have applied our method to representative hexagonal, tetragonal, and trigonal crystals and examined the question of its convergence. The absolute values of the characteristic temperatures obtained here are unreliable because of a lack of 0°K elastic constants for the crystals concerned.

### 1. INTRODUCTION

THE Debye characteristic temperature,  $\Theta_0$ , of nonisotropic crystals may be evaluated by the method of Grüneisen and collaborators<sup>1,2</sup> or by the Hopf-Lechner method<sup>3</sup>; both involve lengthy calculations. There is also a method due to Post.<sup>4</sup> Recently Houston's method<sup>5</sup> for integrating approximately functions of complete cubic symmetry has been applied by Bhatia and Tauber<sup>6</sup> to evaluate  $\Theta_0$  for cubic crystals. The latter work has been further extended by Betts, Bhatia, and Wyman.<sup>7</sup>

Here we propose an analogous method for crystals having a principal axis of symmetry. Our method involves defining harmonic polynomials of appropriate symmetry, which play the same role as Kubic harmonics in similar work on cubic crystals.<sup>5-7</sup> So far, we have not considered using other functions of appropriate symmetry.

### 2. GENERAL THEORY

The following formula is well known:

$$\Theta_0 = - \left( \frac{3N}{k4\pi V} \right)^{\frac{1}{3}} \left[ \sum_{i=1}^3 \int \{v_i(\theta, \varphi)\}^{-3} d\Omega \right]^{\frac{1}{3}}. \quad (1)$$

Here  $N$  is the number of atoms in the solid,  $V$  the volume of the crystal,  $v_i(\theta, \varphi)$  the velocities of the long elastic waves at 0°K, and other symbols have their usual meanings.

We define harmonics  $F_{lm}(\theta, \varphi)$  of a given crystal symmetry group as

$$F_{lm}(\theta, \varphi) = \sum_{m'=-l}^l b_{lm'm} Y_{lm'}(\theta, \varphi), \quad (2)$$

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<sup>1</sup> E. Grüneisen and E. Goens, *Z. Physik* **26**, 250 (1924).

<sup>2</sup> E. Grüneisen and H. Hoyer, *Ann. Physik* **22**, 663 (1935).

<sup>3</sup> L. Hopf and G. Lechner, *Verhandl. deut. physik. Ges.* **16**, 643 (1914).

<sup>4</sup> E. J. Post, *Can. J. Phys.* **31**, 112 (1953).

<sup>5</sup> W. V. Houston, *Revs. Modern Phys.* **20**, 162 (1948).

<sup>6</sup> A. B. Bhatia and G. E. Tauber, *Phil. Mag.* **45**, 1211 (1954). The right-hand side of Eq. (5) in this paper should be multiplied by  $\rho^{-1}$ .

<sup>7</sup> Betts, Bhatia, and Wyman, *Phys. Rev.* **104**, 37 (1956), preceding paper.

where  $l=0, 1, 2, \dots; m=0, \pm 1, \dots \pm l$ ; and where the  $b$ 's are chosen to give combinations of spherical harmonics having the appropriate symmetry. Then any function such as  $f(\theta, \varphi)$ , having the same symmetry, can be expanded in terms of the harmonics  $F_{lm}(\theta, \varphi)$ ,

$$f(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm} F_{lm}(\theta, \varphi), \quad (3)$$

and

$$\frac{1}{4\pi} \int f(\theta, \varphi) d\Omega = a_{00} \equiv a_0. \quad (4)$$

As is well known from the properties of spherical harmonics, Eq. (4) is exact. Our approximation consists of stopping the summation in (3) at a given degree  $l$ . The coefficient  $a_0$  is then found by solving an appropriate number of linear equations found by taking various values of  $(\theta, \varphi)$ .

If dispersion is neglected, the velocities of the elastic waves in nonisotropic crystals,  $v_i(\theta, \varphi)$ , are given by the three roots of the well-known Christoffel equations of elasticity theory.<sup>8</sup> The noncubic crystals considered here have a principal symmetry axis, which we take to be the polar axis  $\theta=0$ . Then the harmonics for a given symmetry are simply "constructed" by choosing those of the functions  $Y_{l,m}(\theta, \varphi) \pm Y_{l,-m}(\theta, \varphi)$  which have the appropriate symmetry. In striking contrast, the construction of harmonics of complete cubic symmetry is a rather involved process.<sup>7</sup> The reason for this is that Kubic harmonics are complicated linear combinations of spherical harmonics.

### Crystals of Symmetry $C_3^h, D_3^h, C_6, D_6, C_6^h, D_6^h$

We shall refer to crystals having any of the above symmetry properties as hexagonal crystals. It is easy to see that the corresponding Christoffel equation is  $\varphi$ -independent and symmetric under  $\theta \rightarrow \pi - \theta$ . Thus the corresponding "cylindrical" harmonics are simply Legendre polynomials of even degree:

$$F_{2l}(\theta, \varphi) = P_{2l}(\cos \theta). \quad (5)$$

<sup>8</sup> A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, p. 299.

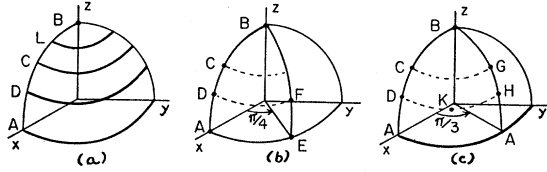


FIG. 1. Illustration of the directions along which the integrand in the formula for Debye  $\Theta_0$  is to be evaluated for (a) hexagonal crystals, (b) tetragonal crystals, and (c) trigonal crystals.

Here, of course, since  $[v_i(\theta, \varphi)]^{-3} \equiv f\rho^{-3}$  is a function of  $\theta$  only, it can be integrated approximately by any of the standard methods. For the sake of uniformity, however, and because of its simplicity, we shall use the method outlined above. A straightforward calculation yields

$$a_0 = [6f_A + f_B + 8f_C]/15, \quad (6.1)$$

$$a_0 = [192f_A + 57f_B + 256f_C + 125f_D]/630, \quad (6.2)$$

$$a_0 = [1368f_A + 153f_B + 1024f_C + 2125f_D + 1000f_L]/5670. \quad (6.3)$$

The integrand  $f$  may be found in the appendix. The directions correspond as follows:  $A \rightarrow (1,0,0)$ ,  $B \rightarrow (0,0,1)$ ,  $C \rightarrow (1,0,1)$ ,  $D \rightarrow (2,0,1)$ ,  $L \rightarrow (1,0,2)$ . These directions are illustrated in Fig. 1(a); the unit sphere is quite evenly covered by them. Equation (6.2) uses all harmonics up to and including those of degree six and so corresponds to the Bhatia-Tauber formula.<sup>6</sup> The other formulas are given so that the convergence of the method can be demonstrated. It should be mentioned that although the choice of directions is somewhat arbitrary, they should be chosen to cover the range of integration fairly evenly. Otherwise we have found that the coefficients occurring in formulas such as (6), for  $a_0$ , nearly cancel one another, leading to poor convergence and hence unreliable results. We stop at  $l=8$  in (3) because Eqs. (6) are found to give sufficiently rapid convergence and because subsequent formulas tend to become somewhat unwieldy.

#### Crystals with Symmetry $D_4$ , $C_4^v$ , $S_4^u$ , $D_4^h$

We shall refer to crystals having any of the above symmetry properties as "tetragonal" crystals. The corresponding Christoffel equation is invariant under  $\theta \rightarrow \pi - \theta$ ,  $\varphi \rightarrow -\varphi$  or  $\varphi \rightarrow \varphi + \pi/2$ . The appropriate "tetragonal" harmonics are thus

$$T_{2l, 4m}(\theta, \varphi) = \cos 4m\varphi P_{2l}^{4m}(\cos\theta), \quad (7)$$

with  $4m \leq 2l$ ;  $l, m = 0, 1, 2, \dots$ . Solving the corresponding equations (3), we find

$$a_0 = [2f_A + f_B + 8f_C + 4f_E]/15, \quad (8.1)$$

$$a_0 = [24f_A + 57f_B + 256f_C + 125f_D + 168f_E]/630, \quad (8.2)$$

$$a_0 = [288f_A + 144f_B + 512f_C - 125f_D + 96f_E + 375f_F]/1260. \quad (8.3)$$

The directions  $A$  to  $D$  have the same meaning as before,  $E \rightarrow (1,1,0)$ , and  $F \rightarrow (1,1,1/\sqrt{2})$ . These directions are illustrated in Fig. 1(b). They are chosen by realizing that the Christoffel equation for the velocities factors only along the arcs  $\varphi=0$ ,  $\varphi=\pi/4$  and  $\theta=\pi/2$  or equivalent arcs. Equation (8.1) is obtained from (3) by ignoring all tetragonal harmonics of degree  $l=6$  or higher. Equation (8.3) is found by ignoring all tetragonal harmonics of degree  $l=8$  or higher. For comparison we also give formula (8.2) for five directions found by leaving out  $T_{64}$  but including  $T_{60}$  in (3). The formulas for the  $f$ 's are again to be found in the appendix.

#### Crystals with Symmetry $D_3$ , $C_3^v$ , $S_6^u$

We shall call crystals with any of the above symmetry properties "trigonal" crystals. The corresponding Christoffel equation is invariant under  $\varphi \rightarrow -\varphi$  or  $\varphi \rightarrow \varphi + \pi/3$  while  $\theta \rightarrow \pi - \theta$ . The appropriate trigonal harmonics are thus

$$A_{2l, 3m}(\theta, \varphi) = \cos 3m\varphi P_{2l}^{3m}(\cos\theta), \quad (9)$$

with  $3m \leq 2l$ ;  $l, m = 0, 1, 2, \dots$ . For trigonal crystals the Christoffel equation unfortunately factors only along the arc  $\varphi=0$  or equivalent directions. Thus we try to choose as many as possible of the directions along this arc.

Using all four  $A_{2l, 3m}$  of degree four or less leads to

$$a_0 = [6f_A + f_B + 4f_C + 4f_G]/15, \quad (10.1)$$

where direction  $G \rightarrow (1,0,1)$  (equivalent to direction  $\varphi=\pi/3$  and  $\theta=\pi/4$ ). Including all harmonics of degree six or less except  $A_{66}(\theta, \varphi)$  gives

$$a_0 = [384f_A + 114f_B + 256(f_C + f_G) + 125(f_H + f_D)]/1260, \quad (10.2)$$

where the direction  $H \rightarrow (2,0,1)$ . To use all seven trigonal harmonics of degree six or less requires us to choose a seventh direction for which  $\varphi \neq 0$  in order to be able to solve (3) for  $a_0$ . We take this direction to be  $K \rightarrow (0,2,1)$  and obtain

$$a_0 = [1536f_A + 456f_B + 1024(f_C + f_G) - 625(f_D + f_H) + 2250f_K]/5040. \quad (10.3)$$

The directions chosen for this symmetry class are illustrated in Fig. 1(c). The unit sphere is again quite evenly covered.

### 3. CALCULATION OF $\Theta_0$ AND DISCUSSION

In the previous section we have obtained Bhatia-Tauber type formulas in various approximations for each of the three sets of symmetry classes considered in this paper. In this section we use these formulas to calculate  $\Theta_0$  for several examples of crystals from each symmetry class. These examples include almost all crystals, of these symmetries, for which elastic constants are available. The elastic constants and calculated and

TABLE I. Characteristic temperatures and elastic constants for certain noncubic crystals.

(1) Hexagonal crystals												
Material	Elastic constants in 10 <sup>12</sup> dynes/cm <sup>2</sup>					Source	Characteristic temperatures in °K					Source
	c <sub>11</sub>	c <sub>33</sub>	c <sub>44</sub>	c <sub>12</sub>	c <sub>13</sub>		Θ <sub>0</sub> <sup>1</sup>	Θ <sub>0</sub> <sup>2</sup>	Θ <sub>0</sub> <sup>3</sup>	Grüneisen and Goens <sup>b</sup>	Θ <sub>0</sub> <sup>E</sup>	
Beryl	2.692	2.372	0.6536	0.9644	0.6690	Hearmon <sup>a</sup>	1065	1065	1066		1000	Kittel <sup>1</sup>
Cd	1.146	0.4851	0.1835	0.4364	0.4064	Hearmon <sup>a</sup>	186.3	186.3	186.2		180	Kittel <sup>1</sup>
Cd	1.206	0.5133	0.1852	0.4812	0.4420	Grüneisen and Goens <sup>b</sup>	187.9	187.9	188.0	189	180	Kittel <sup>1</sup>
Co	3.071	3.581	0.7550	1.650	1.027	McSkimin <sup>c</sup>	443.5	443.8	445.6		385	Seitz <sup>m</sup>
Ice	0.1385	0.1499	0.0319	0.0707	0.0581	Humbel <i>et al.</i> <sup>d</sup>	292.3	292.6	293.1		315	Blue <sup>n</sup>
Mg	0.5747	0.5983	0.1669	0.2403	0.1939	Hearmon <sup>a</sup>	363.6	364.4	365.6		290	Seitz <sup>m</sup>
Zn	1.631	0.6111	0.3947	0.3062	0.4911	Hearmon <sup>a</sup>	305.4	307.8	308.3		235	Kittel <sup>1</sup>
Zn	1.610	0.5420	0.4000	0.4320	0.4370	Grüneisen and Goens <sup>b</sup>	301.9	304.2	303.5	305	235	Kittel <sup>1</sup>

(2) Tetragonal crystals													
Material	Elastic constants in 10 <sup>12</sup> dynes/cm <sup>2</sup>					Source	Characteristic temperatures in °K					Source	
	c <sub>11</sub>	c <sub>33</sub>	c <sub>44</sub>	c <sub>66</sub>	c <sub>12</sub>		c <sub>13</sub>	Θ <sub>0</sub> <sup>c</sup>	Θ <sub>0</sub> <sup>1</sup>	Θ <sub>0</sub> <sup>2</sup>	Θ <sub>0</sub> <sup>3</sup>		Θ <sub>0</sub> <sup>E</sup>
Sn	0.8391	0.9665	0.1754	0.07407	0.4870	0.2810	Hearmon <sup>a</sup>	151.9	164.1	165.6	163.1	195	Corak <sup>o</sup>
Zircon	0.7350	0.4600	0.1380	0.1600	0.0900	-0.0540	Bhimasackar <i>et al.</i> <sup>f</sup>	260.0	268.6	268.2	271.8		
KDP	0.7230	0.6180	0.1280	0.0618	0.0439	0.1980	Hearmon <sup>a</sup>	306.2	336.9	338.4	337.6		
NH <sub>4</sub> DP	0.6850	0.3240	0.0861	0.0602	-0.0180	0.0178	Hearmon <sup>a</sup>	743.7	795.4	795.2	797.6		

(3) Trigonal crystals															
Material	Elastic constants in 10 <sup>12</sup> dynes/cm <sup>2</sup>						Source	Characteristic temperatures in °K					Source		
	c <sub>11</sub>	c <sub>33</sub>	c <sub>44</sub>	c <sub>66</sub>	c <sub>13</sub>	c <sub>14</sub>		Θ <sub>0</sub> <sup>c</sup>	Θ̄ <sub>0</sub> <sup>c</sup>	Θ <sub>0</sub> <sup>1</sup>	Θ <sub>0</sub> <sup>2</sup>	Θ <sub>0</sub> <sup>3</sup>		Grüneisen and Hoyer <sup>k</sup>	Θ <sub>0</sub> <sup>E</sup>
Bi	0.8497	0.5943	0.1459	0.1765	0.2860	-0.0573	Hearmon <sup>a</sup>	138.3	122.1	128.3	128.8	127.8		100	Seitz <sup>m</sup>
Corundum	4.650	5.630	2.330	1.750	1.170	1.010	Bhimasackar <sup>b</sup>	867.8	921.3	852.4	893.0	898.8			
Hg	0.3600	0.5051	0.1290	0.0356	0.3030	0.0470	Grüneisen and Sekell <sup>l</sup>	71.57	81.65	73.22	75.84	72.09	69	~60	Kamerlingh Onnes <i>et al.</i> <sup>p</sup>
Quartz	0.8676	1.048	0.5861	0.4021	0.0950	0.1814	Mason <sup>j</sup>	528.3	582.0	553.8	552.9	555.8			
Sb	0.7916	0.4498	0.2852	0.2717	0.2615	0.1060	Hearmon <sup>a</sup>	182.5	205.9	191.7	192.6	193.5		140	Seitz <sup>m</sup>

<sup>a</sup> See reference 9.  
<sup>b</sup> See reference 1.  
<sup>c</sup> See reference 10.  
<sup>d</sup> See reference 11.

<sup>e</sup> See reference 12.  
<sup>f</sup> See reference 13.  
<sup>g</sup> See reference 14.  
<sup>h</sup> See reference 16.

<sup>i</sup> See reference 21.  
<sup>j</sup> See reference 15.  
<sup>k</sup> See reference 2.  
<sup>l</sup> See reference 17.

<sup>m</sup> See reference 18.  
<sup>n</sup> See reference 22.  
<sup>o</sup> See reference 19.  
<sup>p</sup> See reference 20.

experimental values of Θ<sub>0</sub> are listed in Table I.<sup>1,2,9-22</sup> We note that while frequently the elastic constants are only given to two or three significant figures, we use the four-figure values quoted in Table I so that the convergence obtained from our method could be clearly shown, even though the absolute values of the Θ<sub>0</sub>, for the elastic constants used, are only good to about 1%. In some cases stiffness constants were given in the literature and were used to find the elastic constants in the usual manner.

For hexagonal crystals with Christoffel equations that are φ independent, Θ<sub>0</sub><sup>1</sup>, Θ<sub>0</sub><sup>2</sup>, and Θ<sub>0</sub><sup>3</sup> in Table I refer to characteristic temperatures calculated from (1) using (6.1), (6.2), and (6.3), respectively. For

tetragonal crystals Θ<sub>0</sub><sup>1</sup>, Θ<sub>0</sub><sup>2</sup>, and Θ<sub>0</sub><sup>3</sup> have been calculated by using (8.1), (8.2), and (8.3), respectively. For trigonal crystals Θ<sub>0</sub><sup>1</sup>, Θ<sub>0</sub><sup>2</sup>, and Θ<sub>0</sub><sup>3</sup> have been calculated by using (10.1), (10.2), and (10.3), respectively. In the latter two cases we have also obtained Θ<sub>0</sub><sup>c</sup> by assuming the φ dependence of the velocities to be small and using Eq. (6.2). Θ<sub>0</sub><sup>E</sup> refers to the experimental data.

From Table I it can be seen that the various Θ<sub>0</sub> values for a given crystal converge well. However, it is clear from the Θ<sub>0</sub><sup>c</sup> values that the φ dependence of the integrand in (1) must not be neglected. Θ<sub>0</sub><sup>c</sup> was calculated on the assumption that the integrand in (1) is cylindrically symmetrical; the directions A, B, C, and D, along the arc φ=0, are used in (6.2). Θ̄<sub>0</sub><sup>c</sup> corresponds to the use of directions ABGH in (6.2); i.e. to the arc φ=π/3. The values of Θ<sub>0</sub><sup>c</sup> and Θ̄<sub>0</sub><sup>c</sup> differ considerably and even the average of corresponding values yields poor results. We have only given Θ̄<sub>0</sub><sup>c</sup> for trigonal crystals; for tetragonal crystals the results are similar. It is seen, therefore, that the use of the correct harmonic polynomials is thus imperative.

By inspection, it is clear that our formulas yield characteristic temperatures accurate to about 1%. For Hg, the accuracy is about 4%; however, the reason for this lies in the fact that the anisotropy of Hg approaches that of Pb. It is unfortunately not possible to define a measure of anisotropy (corresponding to 2c<sub>44</sub>/(c<sub>11</sub>-c<sub>12</sub>) in cubic crystals) for trigonal crystals. The final formulas are thus significantly superior to the Bhatia-

<sup>9</sup> R. F. S. Hearmon, *Revs. Modern Phys.* **18**, 409 (1946).  
<sup>10</sup> H. J. McSkimin, *J. Appl. Phys.* **26**, 406 (1955).  
<sup>11</sup> Humbel, Jona, and Scherrer, *J. chim. phys.* **50**, C40 (1953).  
<sup>12</sup> The elastic constants for Zn are obtained by averaging the values quoted by Hearmon in reference (7) and those given by C. A. Wert and F. P. T. Tyndall, *J. Appl. Phys.* **20**, 587 (1949).  
<sup>13</sup> J. Bhimasackar and G. Venkataratnam, *J. Acoust. Soc. Am.* **27**, 922 (1955).  
<sup>14</sup> R. F. S. Hearmon, *Brit. J. Appl. Phys.* **3**, 120 (1952).  
<sup>15</sup> W. P. Mason, *Bell System Tech. J.* **30**, 366 (1951).  
<sup>16</sup> J. Bhimasackar, *Proc. Natl. Inst. Sci., India* **16**, 241 (1950).  
<sup>17</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 77.  
<sup>18</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 110.  
<sup>19</sup> W. S. Corak and C. B. Satterthwaite, *Phys. Rev.* **102**, 662 (1956).  
<sup>20</sup> H. Kamerlingh Onnes and G. Holst, *Leiden Comm.* **142C**, 30 (1914).  
<sup>21</sup> E. Grüneisen and O. Sckell, *Ann. Physik* **19**, 387 (1934). The elastic constants of Hg were measured at -190°C.  
<sup>22</sup> R. W. Blue, *J. Chem. Phys.* **22**, 280 (1954).

Tauber formula for cubic crystals and should be compared in accuracy to the formulas developed by Betts *et al.*<sup>7</sup> for cubic crystals by using higher order polynomials. The formulas (6.2), (8.3), and (10.3) for integrating over a unit sphere functions  $f(\theta, \varphi)$  of the three symmetries considered in this paper may also prove useful in other connections. They are being applied here to further discussions of the properties of noncubic crystals. Because of the trouble of evaluating the velocity corresponding to the direction  $K$  for trigonal crystals, it may be convenient in future merely to use (10.2) instead of (10.3) since, in the calculations reported in Table I, the two formulas give nearly the same results.

The disagreement between the theoretical and experimental  $\Theta_0$ 's varies between about 5% and 20%. We believe that the reason for this discrepancy can be attributed to two causes. Firstly it may be noted that the experimental  $\Theta_0$ 's, with the exception of the values for Sn and ice, were not obtained recently and may not correspond to the true  $T^3$  region in the heat capacity data. This possibility is emphasized by the fact that the value of  $\Theta_0$  for Sn given recently by Corak and Satterthwaite<sup>19</sup> differs from that quoted by Seitz<sup>18</sup> and Kittel,<sup>17</sup> from whose books most of our experimental data are taken, by over 30%. We also note, in support of this point, that, with the exception of  $\Theta_0$  for Sn and ice, all our calculated  $\Theta_0$ 's lie above the experimental values.<sup>23</sup> Secondly, with the exception of quartz and Hg, we were forced to use the elastic constants of the crystals listed in Table I obtained at or near room temperature. We believe that elastic constants measured

close to 0°K are not available. Now it has been shown by Bhatia and Horton<sup>24</sup> that in the case of Ag the values of  $\Theta_0$  obtained by using room temperature elastic constants and 0°K elastic constants differ by about 10%. A difference of up to 20% found for the crystals considered in this paper is, therefore, not unreasonable. It is a measure of the uncertainty in the absolute value of the  $\Theta_0$ 's we have calculated. As soon as reliable 0°K elastic constants become available, our formulas can, of course, be used to give reliable characteristic temperatures. The only calculated values available for comparison are those of Grüneisen and Goens<sup>1</sup> for Cd and Zn and Grüneisen and Hoyer<sup>2</sup> for Hg. To enable us to make a meaningful comparison between the calculated values of Grüneisen and Goens<sup>1</sup> and our own, we used two sets of elastic constants for Cd and Zn. One set represents the values used by Grüneisen and Goens<sup>1</sup> while the other is an average over all the available data. The characteristic temperatures obtained by ourselves and Grüneisen and Goens<sup>1</sup> (Zn and Cd) agree well, but this is not surprising since the integration involved for these hexagonal metals is over only one variable. The agreement between our  $\Theta_0$ 's and that of Grüneisen and Hoyer<sup>2</sup> is not so good. We believe that the numerical averaging procedure of the latter authors is not so satisfactory for trigonal as for hexagonal crystals, especially for Hg where the values of  $[v_i(\theta, \varphi)]^{-3}$  differ by a factor of about five. For Zn and Cd this quantity has only about a 50% variation. The extension of our work to higher orders and other crystal symmetries is straightforward, though this will usually involve the solution of nonfactorable cubic equations.

## APPENDIX

### Tetragonal Crystals

$$f_A = [c_{44}]^{-\frac{3}{2}} + [c_{66}]^{-\frac{3}{2}} + [c_{11}]^{-\frac{3}{2}}. \quad (11.1)$$

$$f_B = 2[c_{44}]^{-\frac{3}{2}} + [c_{33}]^{-\frac{3}{2}}. \quad (11.2)$$

$$f_C = \left[ \frac{1}{2}(c_{66} + c_{44}) \right]^{-\frac{3}{2}} + \left[ \frac{1}{4}(c_{11} + 2c_{44} + c_{33}) + \frac{1}{4}\{(c_{11} - c_{33})^2 + 4(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}} \\ + \left[ \frac{1}{4}(c_{11} + 2c_{44} + c_{33}) - \frac{1}{4}\{(c_{11} - c_{33})^2 + 4(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}}. \quad (11.3)$$

$$f_D = \left[ \frac{1}{5}(4c_{66} + c_{44}) \right]^{-\frac{3}{2}} + \left[ \frac{1}{10}(4c_{11} + 5c_{44} + c_{33}) + \frac{1}{10}\{(4c_{11} - 3c_{44} - c_{33})^2 + 16(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}} \\ + \left[ \frac{1}{10}(4c_{11} + 5c_{44} + c_{33}) - \frac{1}{10}\{(4c_{11} - 3c_{44} - c_{33})^2 + 16(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}}. \quad (11.4)$$

$$f_E = [c_{44}]^{-\frac{3}{2}} + \left[ \frac{1}{2}(c_{11} - c_{12}) \right]^{-\frac{3}{2}} + \left[ \frac{1}{2}(c_{11} + 2c_{66} + c_{12}) \right]^{-\frac{3}{2}}. \quad (11.5)$$

$$f_F = \left[ \frac{1}{5}(2c_{11} - 2c_{12} + c_{44}) \right]^{-\frac{3}{2}} + \left[ \frac{1}{10}(2c_{11} + 2c_{12} + 4c_{66} + 5c_{44} + c_{33}) + \frac{1}{10}\{(2c_{11} + 2c_{12} + 4c_{66} - 3c_{44} - c_{33})^2 \\ + 16(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}} + \left[ \frac{1}{10}(2c_{11} + 2c_{12} + 4c_{66} + 5c_{44} + c_{33}) \\ - \frac{1}{10}\{(2c_{11} + 2c_{12} + 4c_{66} - 3c_{44} - c_{33})^2 + 16(c_{13} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{3}{2}}. \quad (11.6)$$

### Hexagonal Crystals

For  $f_A$ ,  $f_B$ ,  $f_C$ , and  $f_D$ , we simply put  $c_{66} = \frac{1}{2}(c_{11} - c_{12})$  in (11.1) to (11.4).

$$f_L = \left[ \frac{1}{10}(c_{11} - c_{12} + 8c_{44}) \right]^{-\frac{3}{2}} + \left[ \frac{1}{10}(c_{11} + 5c_{44} + 4c_{33}) + \left\{ \frac{1}{10}(c_{11} + 3c_{44} - 4c_{33})^2 + 16(c_{13} + c_{44})^2 \right\}^{\frac{1}{2}} \right]^{-\frac{3}{2}} \\ + \left[ \frac{1}{10}(c_{11} + 5c_{44} + 4c_{33}) - \left\{ \frac{1}{10}(c_{11} + 3c_{44} - 4c_{33})^2 + 16(c_{13} + c_{44})^2 \right\}^{\frac{1}{2}} \right]^{-\frac{3}{2}}. \quad (12)$$

<sup>23</sup> Note added in proof.—This argument is supported by the value of  $\Theta_0 = 204^\circ\text{K}$  found recently for Sb by N. M. Wolcott [Bull. Am. Phys. Soc. Ser. II, 1, 289 (1956)].

<sup>24</sup> A. B. Bhatia and G. K. Horton, Phys. Rev. 98, 1715 (1955).

## Trigonal Crystals

$$f_A = [c_{66}]^{-\frac{3}{2}} + [\frac{1}{2}(c_{44} + c_{11}) + \frac{1}{2}\{(c_{44} - c_{11})^2 + 4c_{14}^2\}^{\frac{1}{2}}]^{-\frac{3}{2}} + [\frac{1}{2}(c_{44} + c_{11}) - \frac{1}{2}\{(c_{44} - c_{11})^2 + 4c_{14}^2\}^{\frac{1}{2}}]^{-\frac{3}{2}}. \quad (13.1)$$

$$f_B = 2[c_{44}]^{-\frac{3}{2}} + [c_{33}]^{-\frac{3}{2}}. \quad (13.2)$$

$$f_C = [\frac{1}{2}(c_{66} + c_{44} - 2c_{14})]^{-\frac{3}{2}} + [\frac{1}{4}(c_{11} + 2c_{44} + 2c_{14} + c_{33}) + \frac{1}{4}\{(c_{11} + 2c_{14} - c_{33})^2 + 4(c_{14} + c_{13} + c_{44})^2\}^{\frac{1}{2}}]^{-\frac{3}{2}} \\ + [\frac{1}{4}(c_{11} + 2c_{44} + 2c_{14} + c_{33}) - \frac{1}{4}\{(c_{11} + 2c_{14} - c_{33})^2 + 4(c_{14} + c_{13} + c_{44})^2\}^{\frac{1}{2}}]^{-\frac{3}{2}}. \quad (13.3)$$

$$f_D = [\frac{1}{2}(4c_{66} + c_{44} - 4c_{14})]^{-\frac{3}{2}} + [\frac{1}{10}(4c_{11} + 4c_{14} + 5c_{44} + c_{33}) + \frac{1}{10}\{(4c_{11} + 4c_{14} - 3c_{44} - c_{33})^2 + 4(4c_{14} + 2c_{13} + 2c_{44})^2\}^{\frac{1}{2}}]^{-\frac{3}{2}} \\ + [\frac{1}{10}(4c_{11} + 4c_{14} + 5c_{44} + c_{33}) - \frac{1}{10}\{(4c_{11} + 4c_{14} - 3c_{44} - c_{33})^2 + 4(4c_{14} + 2c_{13} + 2c_{44})^2\}^{\frac{1}{2}}]^{-\frac{3}{2}}. \quad (13.4)$$

$$f_G = f_C \text{ (with the sign of } c_{14} \text{ changed)}. \quad (13.5)$$

$$f_H = f_D \text{ (with the sign of } c_{14} \text{ changed)}. \quad (13.6)$$

$$f_K = \sum_{i=1}^3 y_i^{-\frac{3}{2}}, \quad (13.7)$$

where the  $y_i$  are solutions of the equation

$$\begin{vmatrix} (4c_{66} + c_{44})/5 - y & -4c_{14}/5 & -4c_{14}/5 \\ -4c_{14}/5 & (4c_{11} + c_{44})/5 - y & (2c_{13} + 2c_{44})/5 \\ -4c_{14}/5 & (2c_{13} + 2c_{44})/5 & (4c_{44} + c_{33})/5 - y \end{vmatrix} = 0.$$

## Surface Conductance and the Field Effect on Germanium\*

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Measurements of the steady-state surface conductance and the change in this conductance with transverse electric field (field effect) have been made on a free germanium surface as a function of the gaseous ambient. The results can be understood in terms of two sets of surface states: one dependent upon the gaseous ambient and with a large density and long time constants, probably located at the outer surface of an oxide layer, and the other a set with much smaller density but shorter time constants, probably located at the germanium-germanium oxide interface. The interface states consist of a discrete state with free energy 0.13–0.15 ev below the intrinsic Fermi energy and density  $1-3 \times 10^{11}$  states/cm<sup>2</sup>, and a small continuous distribution. There is also indication of a discrete state greater than 0.13 ev above the intrinsic Fermi energy. The measurements suggest that surface scattering effects become important for large barrier layers.

## I. INTRODUCTION

CONSIDERABLE progress<sup>1-19</sup> has been made in recent years in understanding the nature of the space-charge layer at a germanium surface and the way

\* The experiments to be reported here were initiated by S.R.M. and J.B. The results were reported in part in reference 2 and more completely by Morrison, Sun, and Bardeen in a technical report, January 15, 1955 (unpublished). Because of uncertainties in the calibration of the field effect measurements, the results were only of qualitative value. The apparatus was revised by J.R.S., and further measurements made are reported by J. R. Schrieffer and J. Bardeen in a technical report, April 10, 1955 (unpublished). Further revisions in the equipment, particularly to increase the temperature stability, were made by R.E.C. The work was supported by the Office of Naval Research and by a grant from Motorola, Inc.

<sup>1</sup> W. H. Brattain and J. Bardeen, *Bell System Tech. J.* **32**, 1 (1953).

<sup>2</sup> J. Bardeen and S. R. Morrison, *Physica* **20**, 873 (1954).

<sup>3</sup> C. G. B. Garrett and W. H. Brattain, *Phys. Rev.* **99**, 376 (1955).

it varies with ambient and with surface treatment. There is good evidence that the surface barrier results from two different types of surface states with radically

<sup>4</sup> E. N. Clarke, *Phys. Rev.* **91**, 756 (1953); **94**, 1420 (1954).

<sup>5</sup> S. R. Morrison, *J. Phys. Chem.* **57**, 860 (1953).

<sup>6</sup> W. Shockley and J. L. Pearson, *Phys. Rev.* **74**, 232 (1948).

<sup>7</sup> P. Handler, *Bull. Am. Phys. Soc. Ser. II*, **1**, 144 (1956).

<sup>8</sup> G. G. E. Low, *Proc. Phys. Soc. (London)* **B68**, 10 (1955).

<sup>9</sup> H. C. Montgomery and B. A. McLeod, *Bull. Am. Phys. Soc. Ser. II*, **1**, 53 (1956).

<sup>10</sup> J. R. Schrieffer, *Phys. Rev.* **94**, 1420 (1954); **97**, 641 (1955).

<sup>11</sup> W. L. Brown, *Phys. Rev.* **98**, 1565 (1955).

<sup>12</sup> Stutz, de Mars, Davis, and Adams, *Phys. Rev.* **101**, 1272 (1956).

<sup>13</sup> de Mars, Stutz, and Davis, *Phys. Rev.* **98**, 539 (1955).

<sup>14</sup> Stutz, Davis, and de Mars, *Phys. Rev.* **98**, 540 (1955).

<sup>15</sup> R. H. Kingston, *Phys. Rev.* **98**, 1766 (1955); **93**, 346 (1954).

<sup>16</sup> W. L. Brown, *Phys. Rev.* **91**, 518 (1953).

<sup>17</sup> W. L. Brown, *Phys. Rev.* **100**, 590 (1955).

<sup>18</sup> W. L. Brown, *Bull. Am. Phys. Soc. Ser. II*, **1**, 48 (1956).

<sup>19</sup> H. A. Gebbie and K. Blodgett, *Phys. Rev.* **100**, 970 (1955).