theory if the structure factor is considered to decrease with increasing temperature.

It may be generally concluded, that under the conditions of the present experiment, thermal motion does not affect diffraction as a structural imperfection. Contrary to the effects of structural imperfections, both integrated intensities and half-widths decrease with increased thermal motion.

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Vibrational Amplitudes in Germanium and Silicon

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From the temperature dependence of x-ray Bragg reflections, Debye temperatures related to vibrational amplitudes Θ_M of 290±5°K and 543±8°K were determined for germanium and silicon, respectively. These are lower by about 20% than the corresponding specific-heat Debye temperatures Θ_D and consequently give mean square amplitudes 40% greater than those calculated from specific heat measurements.

The large difference between the two types of Debye temperatures can be explained in terms of the normal mode frequency spectrum. The low Θ_M values result because the lower frequency modes contribute proportionally more to the vibrational amplitudes than to the specific heat.

INTRODUCTION

The present investigation was undertaken in conjunction with a general study of the effect of thermal motion on diffraction from perfect single crystals of germanium and silicon.[1] In order to establish the form of the perfect-crystal Debye-Waller factor, it is necessary to know the mean square vibrational amplitude at a given temperature. It does not necessarily follow that this quantity can be accurately determined from a Debye temperature $\Theta_D(T)$ determined from specific-heat measurements. It is a well established fact that the x-ray integrated intensity of an ideally imperfect crystal is proportional to the Debye-Waller factor $\exp(-2M)$, where M is proportional to the mean square vibrational amplitude $\langle u^2\rangle$. In this work we have measured the temperature dependence of the Bragg reflections of ideally imperfect powders of germanium and silicon to arrive at values for M. To conveniently express the results of this type of measurement it has been customary to make a comparison with the Debye theory of lattice vibrations. This allows one to express M and $\langle u^2\rangle$ in terms of a single parameter $\Theta_M(T)$ the Debye temperature related to vibrational amplitudes. Because the frequency spectrum is weighted in different ways, $\Theta_M(T)$ and $\Theta_D(T)$ will not necessarily be the same. We will compare experimental values of Θ_M and Θ_D with those expected from an approximate normal mode spectrum calculated from dispersion curves determined from neutron scattering.

EXPERIMENTAL

In an effort to assure that the silicon and germanium samples used in the experiment diffracted as ideally imperfect crystal powders, very finely divided material was prepared, from which powder briquettes were then pressed. The silicon was ground in a ball mill and washed in HCl and HF to remove iron and SiO_2. Germanium powder was obtained by hydrogen reduction of germanium oxide at 750°C. About 85% of the Si particles were under 5 μ in size. The germanium was somewhat finer than the silicon. This small particle size is helpful not only in reducing extinction, but also in improving the randomness of orientation in the pressed samples.

Integrated intensity measurements were made of the (422), (440), and (531) reflections of silicon and of the (400), (422), (511–333), (440), and (531) reflections of germanium as a function of temperature at and above room temperature using crystal monochromated Cu $K\alpha$ radiation and a scintillation counter spectrometer. The samples were heated in a furnace on the spectrometer using a purified helium atmosphere. The measurements on silicon were carried to a temperature of 900°C and on germanium to 850°C.

The characteristic temperature Θ_M is related to the temperature dependence of the integrated intensities through Debye-Waller theory. The exact relation is

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[1] B. W. Batterman, Phys. Rev. **126**, 1461 (1962); and previous paper [Phys. Rev. **127**, 686 (1962)].

given in an earlier article[2] and will not be reproduced here. This relation, however, can be simplified with sufficient accuracy for the present case. Because of the unusually low values of the thermal expansion coefficients, changes with temperature in density, Lorentz-polarization factor, and scattering factor due to lattice expansion are negligible for both silicon and germanium. Also negligible is the temperature dependence of Θ_M as calculated from Paskin's modification of the Zener-Bilinsky theory[3] in the temperature range between 300° and 1100°K.[4] Under the above assumptions, the integrated intensity of a Bragg reflection is proportional to the modified Debye-Waller factor $\exp[-2M(1-\beta)]$, where

$$M=(6h^2T/mk\Theta_M{}^2)[\varphi(x_m)+\tfrac{1}{4}x_m]\sin^2\theta/\lambda^2 \tag{1}$$

and the factor β is a correction for the contribution of thermal diffuse scattering to the integrated intensity.[5] β lies between 0.02 and 0.03 for the reflections considered here. Making use of the first two terms of the series expansion of the Debye function, $\varphi(x_m)+x_m/4=\psi(x_m)=1+(x_m/6)^2$, and noting that $x_m=\Theta/T$, we can write

$$\ln R-A(T-T_0)(36TT_0)^{-1}=A(T_0-T)\Theta_M{}^{-2}, \tag{2}$$

Table I. Experimental values of Θ_M obtained from the slopes of Figs. 1 and 2.

(*hkl*)	Θ_M silicon (°K)	Θ_M germanium (°K)
(400)		289±10
(422)	555±13	288±10
(511-333)		295±10
(440)	555±16	286±10
(531)	520±9	290±10
Average all reflections	543±8	290±5

where R is the ratio of the integrated intensity at temperature T to that at reference temperature T_0 and

$$A=(12h^2/mk)(\sin\theta/\lambda)^2(1-\beta). \tag{3}$$

If the second term in Eq. (2) (which is small compared to unity) is abbreviated by δ, the equation can be rewritten as

$$\ln[R(1-\delta)]=A(T_0-T)\Theta_M{}^{-2}. \tag{4}$$

Figures 1 and 2 give the experimental results. Here $\ln R(1-\delta)$ is plotted vs T so that the slope of the curves is directly $A/\Theta_M{}^2$. Table I gives the resulting values for Θ_M. The error bars in Figs. 1 and 2 give the statistical counting error of each point. The errors given in Table I represent the uncertainty in determining the slopes from Figs. 1 and 2.

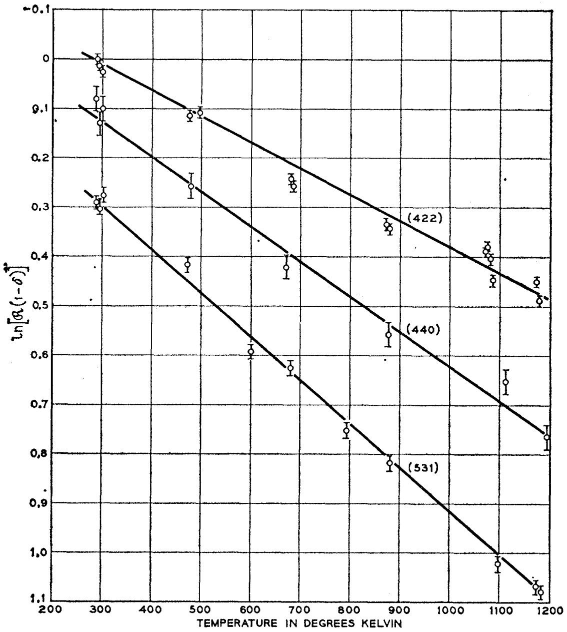

Fig. 1. Logarithm of integrated intensity vs temperature of the (422), (440), and (531) powder reflections of silicon.

The silicon and germanium powder samples must exhibit negligible extinction if the temperature dependence of integrated intensity is to depend on $\exp(-2M)$ as we have assumed. As a check on this important point, the measured intensities were com-

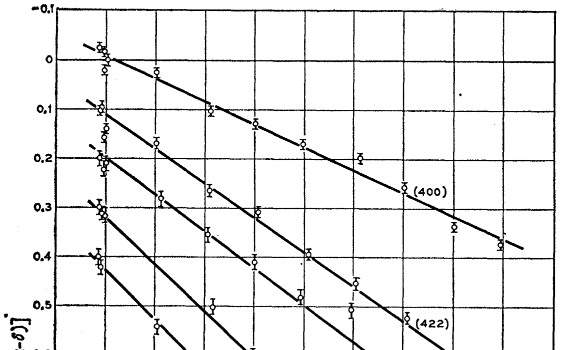

Fig. 2. As in Fig. 1 but for the (400), (422), (511-333), (440), and (531) reflections of germanium.

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[2] D. R. Chipman, J. Appl. Phys. **31**, 2012 (1960).

[3] A. Paskin, Acta Cryst. **10**, 667 (1957).

[4] Neglect of these corrections results in an error of about 1% in the final value of Θ_M for germanium and about ½% for silicon.

[5] D. R. Chipman and A. Paskin, J. Appl. Phys. **30**, 1998 (1959).

TABLE II. Comparison of experimental and theoretical integrated intensities of germanium and silicon relative to aluminum. Experiment and theory were matched at the (331) reflection of aluminum.

	hkl	Experiment		Theory[a]
Aluminum	331	1.00	↔	1.00
	400	0.30		.31
	420	0.94		.97
Germanium	400	1.40		1.49
	422	2.82		2.99
	333–511	1.56		1.66
	440	0.91		0.98
	531	1.89		1.75
Silicon	422	1.48		1.55
	440	0.48		0.55
	531	0.91		1.04

[a] The theoretical intensities were calculated according to Eq. (1) in reference 5. The form factors for aluminum and silicon were taken from A. J. Freeman, Acta Cryst. 12, 261 (1959) and for germanium *ibid.* 12, 929 (1959).

pared with the intensities from an aluminum powder sample previously shown[6] to be free of extinction. The results of these relative measurements are given in Table II. Since the difference in integrated intensities between mosaic and perfect crystals is the order of a factor of 5 for the measured reflections, the over-all agreement is adequate, and justifies the present treatment based on the mosaic powder formula.

DISCUSSION OF RESULTS

The room temperature values for the specific-heat Debye temperatures $\Theta_D(300°\mathrm{K})$ measured by Flubacher, Leadbetter, and Morrison[7] are 354° and 647°K for germanium and silicon, respectively. These are to be compared with $\Theta_D=290°$ and 543°K for germanium and silicon given in Table I. The large discrepancy between Θ_D and Θ_M should be a result of the departure of the true vibrational spectrum from the parabolic form assumed in the Debye theory. Fortunately, Brockhouse and Iyengar[8] have measured the phonon dispersion curves of germanium with a neutron diffraction technique and Phillips[9] has used these data to compute a frequency spectrum which is reproduced in Fig. 3. The specific-heat Debye temperatures calculated by Phillips from the distribution were in excellent agreement with the heat capacity measurement of Flubacher, Leadbetter, and Morrison in the range of 0° to 200°K. At 300°K the (FLM) value was $\Theta_D(300°\mathrm{K})=354°\mathrm{K}$ while Phillips' theoretical value was 383°K. Our Θ_M for germanium averages 290°K in the range 300° to 1100°K.

The relation between Θ_M and the temperature dependence of the intensity data is given in Eq. (1). M can be given[10] directly in terms of the frequency distribution as

$$M=\frac{2h}{m}\left(\frac{\sin\theta}{\lambda}\right)^2\int F(\nu)\nu^{-1}\left(\frac{1}{2}+\frac{1}{e^x-1}\right)d\nu\bigg/\int F(\nu)d\nu, \quad (5)$$

where $x=h\nu/kT$. Combining Eqs. (1) and (5), it follows that

$$\Theta_M{}^2(T)=\frac{3hT\psi(x)\int F(\nu)d\nu}{k\int F(\nu)\nu^{-1}[\frac{1}{2}+(e^x-1)^{-1}]d\nu}. \quad (6)$$

The integral involved in (6) was evaluated as a function of temperature on a digital computer and Θ_M was determined through iteration of Eq. (6). $F(\nu)$ is taken from the tabulation labeled $F_{\mathrm{II}}(\nu)$ in Phillips' paper.[9] The resulting Θ_M values are given in Fig. 4 together with the Θ_D values calculated by Phillips from the same frequency distribution. (Note the different scales for the two curves.) Our experimental value of $\Theta_M=290\pm5°\mathrm{K}$ is in excellent agreement with the theoretical value of 296°K in the observed temperature range.

This computation shows explicitly that the same frequency distribution will give quite different Debye temperatures depending on the type of measurement. The difference between $\Theta_D=354°\mathrm{K}$ and $\Theta_M=290°\mathrm{K}$ in the vicinity of room temperature is real and can be qualitatively explained in terms of the frequency distribution. Since the diamond structure has two atoms in the unit cell, there exist the optic modes in Fig. 3. For these temperatures where $x_{\max}$ is in the

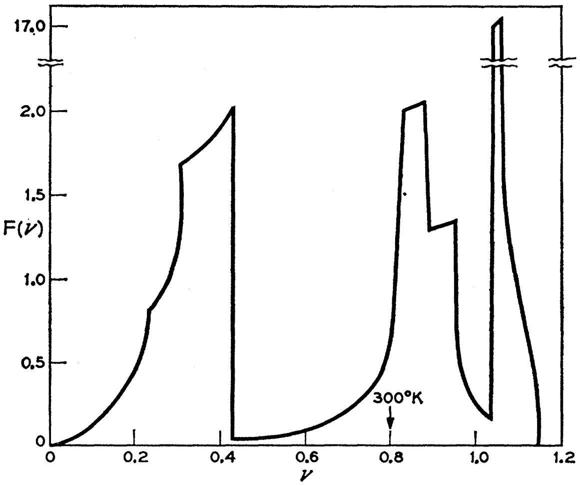

FIG. 3. The frequency distribution of germanium according to Phillips.[9] The frequency scale is reduced by $\Theta_0=372°\mathrm{K}$.

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[6] B. W. Batterman, D. R. Chipman, and J. J. De Marco, Phys. Rev. **122**, 68 (1961).

[7] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. 4, 273 (1959).

[8] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[9] J. C. Phillips, Phys. Rev. **113**, 147 (1959).

[10] M. Blackman, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Part I, Vol. 7, p. 325.

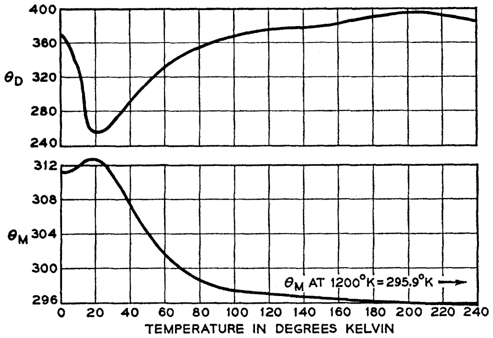

FIG. 4. Comparison of Θ_D and Θ_M calculated from the frequency distribution in Fig. 3.

vicinity of unity or smaller, the energies in each of the normal modes is very nearly kT and each mode contributes essentially the same amount to the specific heat. On the other hand, if one is interested in the mean square amplitude, the contribution is greater for the lower than the higher frequency modes. For the temperature range investigated, the optic modes contribute to the specific heat not much differently than a Debye spectrum with a high Debye temperature. However, the optic mode contribution to the mean square amplitude is very small, and Θ_M is lower than Θ_D because the amplitude is heavily weighted by the low-frequency acoustic modes.

Phillips' calculated Θ_D in the vicinity of room temperature are in disagreement with experiment by about 6% while the agreement below 150°K is better than 1%. Our calculation of Θ_M from Phillips' spectrum agrees with experiment to about 2% in the vicinity of room temperature. This is probably consistent with Phillips' low-temperature specific heat agreement because in both cases the low-frequency modes predominate.

The low Θ_M for silicon with respect to Θ_D can no doubt be explained in terms of the frequency spectrum in a manner similar to germanium. A detailed spectrum was not available to make a comparison.

CONCLUSIONS

In the vicinity of 300°K, the Debye temperatures Θ_M for germanium and silicon related to the mean square vibrational amplitude $\langle u^2 \rangle$ are about 20% lower than the Θ_D value obtained from a specific-heat measurement. Consequently, a calculation of $\langle u^2 \rangle$ would be in error by about 40% if one used a specific-heat Debye temperature.

It has been explicitly shown that this difference between experimental values of Θ_M and Θ_D for germanium can be explained in terms of the normal-mode spectrum calculated by Phillips. The good agreement between theory and experiment is an additional verification of the correctness of Phillips' frequency distribution. The explanation for a similar difference in the two Debye temperatures of silicon can no doubt be made along similar lines.

The experimental values of Θ_M valid in range 300° to 1100°K are 290 ± 5°K and 543 ± 8°K for germanium and silicon, respectively.

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