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Effect of Thermal Vibrations on Diffraction from Perfect Crystals. II. The Bragg Case of Reflection

Boris W. Batterman
Bell Telephone Laboratories, Murray Hill, New Jersey

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It has been experimentally verified in the case of symmetric Bragg reflection from perfect crystals of silicon that integrated intensities decrease as $\exp(-M)$ with increasing temperature. The usual Debye-Waller factor is $\exp(-2M)$ for mosaic crystals. It has been demonstrated to a significance level of 1.5%, that the intrinsic width of a perfect crystal diffraction maximum is smaller at elevated temperatures, i.e., there exists a thermal narrowing. It is concluded that thermal motion does not affect perfect crystal diffraction in the Bragg case as an imperfection.

INTRODUCTION

IN a previous publication[1] we investigated the effects of thermal motion on the anomalous transmission of x rays in perfect crystals. It was shown experimentally that thermal motion manifests itself in the intensity expression through a Debye-Waller term of the form $\exp(-\alpha M)$ where α is 1.3. Intuitively, one would have expected $\exp(-M)$. The present work concerns itself with thermal effects in symmetric diffraction from the face (the Bragg case) of a perfect crystal of silicon.

THEORY

In a series of classic papers Darwin[2] showed that in symmetric reflection from a crystal (where one can neglect absorption) there exists a range of total reflection whose width is given by

$$W_D=2N\lambda^2(e^2/mc^2)|F|\kappa/\pi\sin2\theta. \qquad (1)$$

The integrated intensity is merely the width times unity plus the contributions of the tails, giving

$$R=(E\omega/I)_\sigma=(8/3)\kappa N^2\lambda(e^2/mc^2)|F|/\pi\sin2\theta, \qquad (2)$$

where λ is the x-ray wavelength, (e^2/mc^2) the classical electron radius, N the number of cells with structure factor F per unit volume, and $\kappa=1$ or $|\cos2\theta|$ for the σ and π states of polarization.

It has been tacitly assumed since Darwin's original formulation that thermal motion is to be included by merely replacing F by $F_0\exp(-M)$. A recent treatment by Parthasarathy[3] has lent support to this assumption for the case where absorption can be neglected. Upon heating a perfect crystal one would expect the integrated intensity to decrease according to $\exp(-M)$. On the other hand, for a mosaic crystal, theory and experiment give $\exp(-2M)$. It is well known that the more imperfect a crystal is, the greater is its integrated intensity. In certain cases the integrated intensity diffracted from an ideally imperfect crystal can be as much as a factor of 30 greater than from a perfect crystal. In the sense that thermal motion destroys perfect periodicity, it can be considered an imperfection. In spite of this, diffraction theory predicts that thermal motion should decrease rather than increase the diffracted integrated intensity. Neither this decrease in intensity with temperature, nor the form of the Debye-Waller factor [$\exp(-M)$ or $\exp(-2M)$] has been experimentally verified.

If F in Eq. (1) is replaced by F_0e^{-M}, we get the surprising result that the width of the reflection should decrease with increasing temperature, i.e., there should be a thermal narrowing. There is an interesting physical interpretation to this result. At first glance, it is surprising that an infinite perfect crystal should give rise to diffraction maxima of finite width. In usual diffraction pheonomena, as the number of regularly arranged scattering centers approaches infinity, the widths of the diffraction maxima become infinitesimally small. The reason the perfect-crystal Bragg peaks are finite in width is simply that because of extinction, only a small number of atoms of the essentially infinite crystal contribute to the reflection. The primary beam penetrates only a small distance in the crystal before out of phase multiple reflections extinguish the beam. Thus, the depth of penetration should be related to the width of the maxima.

At the Bragg angle, the primary beam intensity is attenuated with an exponential factor given by[4]

$$\exp[-(e^2/mc^2)\pi N\lambda Ft/2\sin\theta], \qquad (3)$$

where t is the distance perpendicular to the diffracting planes. The exponent is proportional to the amplitude scattered per plane of atoms. Thus, in a distance

$$t_0=[(e^2/mc^2)\pi N\lambda F/2\sin\theta]^{-1} \qquad (4)$$

the beam has been reduced by $1/e$. The distance t_0 can then be likened to an effective particle size measuring the number of scattering centers contributing to the diffraction. The breadth of diffraction maxima from a finite crystallite diffracting kinematically (i.e., as an ideal mosaic) is given by the Scherrer formula[5]

$$\beta=K\lambda/\mathrm{d}\cos\theta, \qquad (5)$$

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[1] B. W. Batterman, Phys. Rev. **126**, 1461 (1962).

[2] C. G. Darwin, Phil. Mag. **27**, 315 and 675 (1914).

[3] R. Parthasarathy, Acta. Cryst. **13**, 802 (1960).

[4] R. W. Jame, *The Optical Principles of the Diffraction of X Rays* (G. Bell and Sons, London, 1950) p. 60.

[5] Reference 4, p. 60.

where d is a characteristic linear dimension of the particle and K is a constant which is determined by the actual shape of the particle. If t_0 now is substituted for d, the half-width becomes

$$\beta = K(e^2/mc^2)\pi N\lambda^2 F/\sin 2\theta \qquad (6)$$

and this now has the identical functional form as the Darwin half-width in Eq. (1). In a quantitative way then, the finite width of the Darwin curve is in effect a particle size broadening.[6]

The physical reason for the thermal narrowing is then as follows: As the crystal is heated, F decreases because of the Debye-Waller factor, the scattering amplitude per plane decreases, and correspondingly t_0 increases. The x rays see more atoms of the crystal (the effective particle size increases) and the diffraction maximum becomes narrower.

On the other hand, one may argue loosely that thermal motion will make the planes undulate and consequently extend the angular range over which the planes will diffract. It was one of the purposes of this experiment to determine which view is correct.

Although the absorption of characteristic molybdenum radiation is small in silicon, the correction to the Darwin formula, Eq. (2), for the higher orders is appreciable. The correct expression including absorption has been given by Prins[7] and is included in Eq. (2) by replacing the factor 8/3 by $\int R(k)dk$.[8]

EXPERIMENTAL

The spectrometer, detector, and the crystal furnace have been described in reference 1. The crystals used in the investigation were dislocation-free silicon[9] pulled from the melt and contained about 10^{15} oxygen atoms per cc. The crystals were cut to within about 0.2° of the desired orientation and etched in CP-8 [10] until the surface damage was removed. Figure 1 gives a sketch of the crystal mount. It is essential that the crystal undergo no thermally induced strain either due to external restraints or to temperature differences within the specimen. The crystal was cut so that two small arms projected parallel to the face. These were inserted in holes in the quartz supports which were larger than the arms on the crystal. In this way, the crystal was not gripped rigidly by the support but was still held firmly enough so that it could not be moved easily. The measurements of the (555) and (444) reflections were performed with the furnace evacuated to 10^{-5} mm of mercury. The (660) reflection was measured in an atmosphere of purified helium.

The molybdenum tube was run at approximately 40 kV and 15 mA. Long- and short-wavelength harmonics were eliminated by the use of appropriate filters. The investigated reflections have half-widths less than a second of arc. To improve the precision of the integrated intensity measurements the crystals were detuned from parallelism in the vertical plane. This broadened the reflections to approximately 3–5 sec. This broadening does not affect the integrated intensity but reduces errors due to fluctuations in the angular velocity of the crystal drive. To give good statistics, about ten measurements of the integrated intensity were recorded at each temperature.

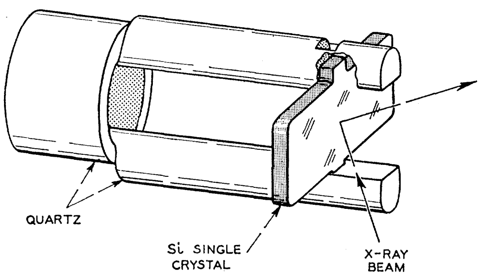

FIG. 1. Sketch of crystal mount.

RESULTS AND DISCUSSION

A. Integrated Intensities

Two silicon crystals were investigated; one for symmetric reflection from the (555) and (444) planes and the other for the (660).

In the Debye model the quantity M appearing in $\exp(-M)$ is given by

$$M = 12h^2T[\varphi(x)+\tfrac{1}{4}x](\sin\theta/\lambda)^2/mk\Theta_D{}^2,$$

where h is Planck's constant, m the mass of the silicon atom, k Boltzman's constant, Θ_D the Debye temperature, and $\Psi = \varphi(x)+\frac{1}{4}x$ the well-known Debye function. Thus, if the temperature behavior of the intensity is $\exp(-M)$, a plot of $\ln R$ vs $T\Psi$ should be linear with a slope inversely proportional to the square of the Debye temperature. The Ψ function is a slowly varying function of both crystal and Debye temperatures. The experimental results for the (444), (555), and (660) reflections of silicon are given in Fig. 2. Ψ is evaluated for three Debye temperatures 500°, 600°, and 700°K. The error bars correspond to ±2% of the observed intensities. Any affect on the slope of the function Ψ is negligible compared to scatter in the data points. The intensities have been corrected for the small variation with temperature of $\int R(k)dk$ (substituted for 8/3) in Eq. (2). On the assumption of an $\exp(-M)$ behavior, one obtains from the slopes, the Debye temperatures for the three measurements given in Table I.

The average Θ_D is 545±20 and is within error, the same in the [111] and [110] directions. In order to ascertain whether the behavior is $\exp(-M)$ or $\exp(-2M)$, one has to compare the Θ_D from the present x-ray data with that of other methods. The specific

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[6] The comparison of the Darwin half-width with a particle size broadening was first made by Professor B. E. Warren.

[7] J. A. Prins, Z. Physik **63**, 477 (1930).

[8] B. W. Batterman, J. Appl. Phys. **30**, 508 (1959).

[9] We are indebted to J. R. Patel for supplying these crystals.

[10] 5:3:3 volume parts HNO_3, glacial acetic acid, 49% HF.

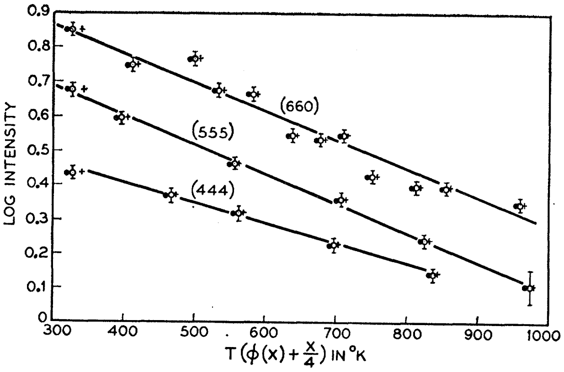

FIG. 2. Log intensity (in arbitrary units) vs $T[\varphi(x)+x/4]$ for the (444), (555), and (660) reflections of silicon. The three points associated with each intensity are for different values of $[\varphi(x)+\frac{1}{4}x]$. The points correspond to assumed values of Θ_D of 500°, 600°, and 700°K, respectively. The relative intensities of each reflection are arbitrary.

heat Θ_D obtained by Flubacker, Leadbetter, and Morrison[11] gives for silicon at room temperatures a Debye temperature of 650°K which is 100°K higher than the present x-ray value obtained assuming $\exp(-M)$. If the Θ_D is calculated assmuing $\exp(-2M)$ the experimental value would be raised by a factor $\sqrt{2}$ giving 771°K. Thus, from the slopes of Fig. 2 and the specific-heat Debye temperature as measured in (8), one cannot decide whether the behavior of the integrated intensity for a perfect crystal is $\exp(-M)$ or $\exp(-2M)$.

It has been verified experimentally and theoretically that the Debye-Waller factor for a mosaic powder is $\exp(-2M)$. Consequently, it is possible to obtain an experimental value for M from x-ray measurements alone. The frequency distribution of normal modes is weighted differently in an x-ray measurement than in a specific-heat determination. Using an x-ray value for the Debye temperature to calculate M, one can establish the form of the temperature factor irrespective of any discrepancy between x-ray and specific-heat Debye temperatures.

In a separate measurement[12] the temperature behavior of the (422), (440), and (531) powder lines of silicon were measured between room temperature and about 850°C. The x-ray Debye temperature determined from the slopes of the intensity vs temperature curves was $\Theta_D=530\pm15$°K. This is in good agreement with the perfect-crystal results assuming $\exp(-M)$. Göttlicher and Wölfel[13] in their measurements on silicon powder report an experimental Debye-Waller factor consistent with a Debye temperature of 546°K which is in good agreement with the present x-ray value for single crystals and powders. There is, however, a discrepancy of about 100°K between the Θ obtained from x-ray and specific-heat measurements.

B. Half-Width as a Function of Temperature

Ideally, the true width of the Bragg peak could easily be obtained if one could employ as a primary beam one which is highly monochromatic and whose angular width is small compared to that of the reflection to be measured. The next best approach is to use the well-known double-crystal spectrometer where one obtains not the true width, but the width of the convolution of the true curves of each of the crystals. If the object is to measure the convoluted width as a function of temperature, both crystals of the spectrometer must be at the same temperature. If the temperatures were not the same, the difference in lattice parameters of the two crystals would disperse the intrinsic wavelength spread in the characteristic K_α lines and broaden the reflection. The experimental difficulties would be more than doubled if one had to heat both crystals to about 500°C yet maintaining thermal stresses so low as to produce no lattice bends greater than a fraction of a second of arc.

We have heated only the second crystal of the spectrometer and have calculated the expected broadening due to wavelength dispersion. If the reflection curve of each of the identical crystals is Gaussian with full width at half maximum equal to W, it can be shown that the convoluted width is simply $\sqrt{2}W$.[14] We have considered the case where the two crystals have different reflection curves and slightly different lattice parameters. It is then necessary to consider the wavelength distribution in the characteristic K_{α_1} line. We assume the α_1 line can be represented as a Gaussian with width at half maximum W_λ.

The result of the triple convolution of the three Gaussian broadening functions gives for the observed half-width

$$W=(W_1^2+W_2^2+W_\lambda^2y^2)^{\frac{1}{2}}, \qquad (7)$$

where

$$y=\sec^2\theta\,\tan\theta\,(\Delta d/d)(1/\lambda). \qquad (8)$$

$\Delta d/d$ is the relative lattice expansion for the heated crystal. $\Delta d/d$ is obtained from the observed $\alpha_1-\alpha_2$ separation at the high temperature and the relation $\Delta\theta=(\Delta\lambda/\lambda)(\Delta d/d)\tan\theta\sec^2\theta$, where $\Delta\lambda$ is the α_1, α_2 wavelength separation and $\Delta\theta$ the observed angular difference in the parallel position of the spectrometer.

TABLE I. Experimental values of Θ_D obtained from the slope of Fig. 2.

hkl	Θ_D(°K)
(444)	547±20
(555)	548±20
(660)	540±20

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

[12] The results are reported in B. W. Batterman and D. R. Chipman, following paper [Phys. Rev. **127**, 690 (1962)].

[13] S. Göttlicher and E. Wölfel, Z. Elektrochem. **63**, 891 (1959).

[14] Reference 4, p. 317.

(The $\Delta d/d$ obtained this way agreed quite well with the value calculated from the thermal expansion coefficient of silicon.)

The width of the Darwin curve [Eq. (1)] for the (660) reflection (σ polarization) is calculated to be 0.303 sec of arc at room temperature and with an e^{-M} dependence would be 0.196 sec at 478°C. W_λ for Mo $K\alpha_1$ is 0.29 x units.[15] The thermal expansion coefficient as determined from the $\alpha_1 - \alpha_2$ separation is 3.92×10^{-6} per °C. With these values, and a second crystal temperature of 478°C, Eq. (7) predicts a half-width $W=\sqrt{2}W_1(0.90)$, where $\sqrt{2}W_1$ is the half-width when both crystals are at room temperature. Thus, in spite of the wavelength broadening, the convoluted half-width is predicted to be about 10% narrower at 478°C than at room temperature. The calculated narrowing of 10% is due to the combination of approximately a 16% narrowing of the heated crystal and a 5% broadening due to wavelength dispersion.

The assumption of Gaussian line shapes is of course, not strictly correct and consequently the quantative aspects of the calculation should not be taken too seriously. The results do show that broadening due to the natural wavelength spread of the α_1 line is probably smaller than the intrinsic narrowing that theory indicates.

In the experiment, the α_2 line is eliminated by a beam stop at the counter. Although the α_1 and α_2 lines overlap in terms of the crystal angle θ (see Fig. 3) they are separated in space. A typical curve at the high temperature with and without the α_2 stop is shown in Fig. 3. The crystal was rotated at a uniform velocity of 1.2 sec of arc per min and the count rate was traced out on a chart recorder. The half-widths were determined directly from the chart. Because of the extremely narrow linewidth of the (660), the precision of a single peak was not great. The sources of fluctuation included the lack of uniformity in the angular velocity of the crystal drive and the time varying thermal expansion effects of the crystals and the spectrometer. A 1°C change in temperature would shift the peak by its full width. Five experimental runs were made cycling between room temperature and 478°C. In all, 48 peaks were recorded at room temperature and 31 at 478°C. The statistics of the data are given in Table II.

TABLE II. Numerical values for "t" test of half-width data. N refers to the number of determinations at the given temperature.

	20°C	478°C
$\langle W\rangle$ (sec)	0.538	0.505
N	48	31
$(\Sigma\sigma^2)/(N-1)$	0.00402	0.00387
$t=2.27$		

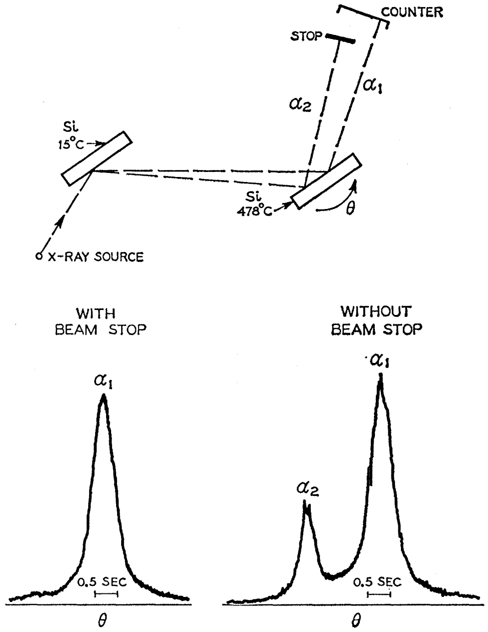

FIG. 3. Reflection curves for (660) reflection of silicon. The insert indicates how the α_2 line is eliminated when the crystals are at different temperatures.

The difference between the average values at the two temperatures is 2.27 times the standard error of the difference. According to a standard t test this would lead to rejection of the hypothesis that the two half-widths are equal at a significance level of 2.9%. In other words, if the two half-widths were equal, one would obtain a difference as large or larger than is observed with a probability of 3 in 100. On this basis, we accept the observed difference to be real. We have thus demonstrated the existence of thermal *narrowing* at a significance level of $2.9/2=1.5\%$. If the intrinsic half-widths W_1 and W_2 were in reality equal at room temperature and 478°C, we would have expected a 5% broadening at the higher temperature due to wavelength dispersion. Thus, the significance level on the hypothesis of thermal narrowing is even lower than 1.5%.

CONCLUSIONS

These measurements have shown that the integrated intensity of a perfect crystal of silicon diffracting in the Bragg case decreases with increasing temperature. The rate of decrease is exponentially half as great as that of silicon powder. Thus, it may be concluded that the Debye-Waller factor for perfect crystals diffracting in symmetric Bragg reflection is e^{-M} compared to a value of e^{-2M} for the ideally imperfect crystal.

We have shown to a statistical significance level of 1.5% that the half-width of a perfect crystal reflection decreases with increasing temperature, i.e., there exists a thermal narrowing in the symmetric Bragg case. The narrowing can be predicted from the simple Darwin

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[15] A. H. Compton and S. K. Allisson, *X Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1935), p. 745.

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

Boris W. Batterman
Bell Telephone Laboratories, Murray Hill, New Jersey

AND

David R. Chipman
Ordnance Materials Research Office, Watertown, Massachusetts

(Received March 7, 1962)

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)].