number of figures '1' in the Zhdanov symbol as well as their distribution among the even and odd places of the symbol may be directly obtained with certain limits of error from the values $\pi(0,2)$, $\pi(1,3)$, and $\pi(-1,3)$ obtainable from the set of $|S|^2$ values.

As the examples show, the application of the mode of procedure advocated by Mardix *et al.* may lead to erroneous conclusions for the cyclicity.

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A Neutron Diffraction Search for Non-centrosymmetric Thermal Oscillations in Germanium and Silicon*

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A neutron diffraction study was made of the 222 reflection of germanium and silicon between the temperatures of 25 and 500°C. Care was taken to reduce effects of simultaneous and higher order reflections. Extinction effects were considered, as nearly perfect crystals were employed in the study. Within the sensitivity of the experiment, no 222 neutron intensity was detected. The resulting upper limit placed on β, the cubic atomic potential constant, is roughly one half of a previously suggested value.

Introduction

The inclusion of an anticentrosymmetric potential constant β as a perturbation in the usual Einstein model derivation of the Debye–Waller factor has been used to accurately describe the unique temperature dependence of the strengths of certain reflections of UO_2, CaF_2, and BaF_2 as observed in the neutron diffraction work of Willis (1963*a*,*b*, 1965). Dawson & Willis (1967) have further suggested that the anticentrosymmetric site symmetry of diamond structured crystals also allows the existence of such an anharmonic term in the binding potential experienced by each atom.

In such crystals, inclusion of this term in the derivation of the Debye–Waller factor results in a non-zero structure factor for the forbidden reflections ($h+k+l=4n+2$, $n=0,1,2,\ldots$) of the form

$$F_{hkl}\exp\{-M(T)\}=-i8b\left(\frac{\pi}{a_0}\right)^3\left(\frac{\beta}{\alpha^3}\right)(hkl)(\mathrm{k}T)^2 \exp\left\{-\frac{\pi^2\mathrm{k}T}{\alpha}\left(\frac{h^2+k^2+l^2}{a_0^2}\right)\right\} \quad (1)$$

(where β is a small perturbation on the harmonic potential constant α). In the above equation, b is the nuclear scattering length of the atom, a_0 the cube edge, k Boltzmann's constant, T the absolute temperature, and h, k, l, the Miller indices of the reflection involved. The exponential is the harmonic Debyc–Waller factor. This structure factor is purely imaginary (from symmetry considerations only; this does not imply an attenuation factor), and is directly proportional to the anticentrosymmetric potential constant β, the product of the Miller indices, and the square of the absolute temperature. The effect should thus be strongest at high temperatures in forbidden reflections of high order.

One may reproduce the above in the formalism of quantum mechanics, by tetrahedrally perturbing a spherical harmonic oscillator. Such an approach predicts a non-zero structure factor when $T=0$°K due to zero state motion. When T is greater than one quarter of the Debye temperature of the materials, however (the Debye temperatures of silicon and germanium reported by Batterman & Chipman (1962) are 543 and 290°K respectively), the classical and quantum mechanical predictions are indistinguishable.

Interaction of the neutrons with the anticentrosymmetrically distributed binding electrons of these materials would also produce Bragg scattering in otherwise forbidden reflections, Such interactions, however, are very weak (Krohn & Ringo, 1966; Obermair, 1967), and can safely be ignored here.

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On the basis of the fluorite work, Dawson & Willis (1967) have suggested 10^{-11} erg.Å^{-3} as a possible value for β in germanium and silicon. Using values of α determined from the Debye temperatures of these materials ($\alpha = 2{\cdot}89 \times 10^{-12}$, and $3{\cdot}93 \times 10^{-12}$ erg.Å^{-2} for germanium and silicon respectively), we see that equation (1) predicts $F_{222}/F_{111} \simeq 1/400$ at $T = 300\,^{\circ}\mathrm{K}$. Though previous room temperature work (Collela & Merlini, 1966) was not sufficiently sensitive to observe this, we felt that a careful experiment at elevated temperatures could provide a good test of this number.

Experimental

We have sought to measure the neutron integrated reflectivity of the 222 forbidden reflection of germanium and silicon at temperatures between 20 and 500 °C. In attempting to detect the extremely low intensity expected in these reflections, one must minimize possible interfering effects, such as higher order Bragg reflections, and simultaneous Bragg events.

The probability of a double Bragg event (in which one or more reflections can occur simultaneously with the reflection under study, adding or subtracting intensity from it) increases greatly with the order of the reflection under study (Moon & Shull, 1964). To avoid such events, we were limited to the forbidden reflection of lowest order (with non-zero indices), the 222 reflection. For this reflection, we sought a crystal azimuthal orientation and wavelength to cube edge ratio which would be free of double Bragg occurrences, while allowing us to use the most intense portion of the reactor spectrum (neutron wavelengths between 0·5 and 2·5 Å). We chose the values $\lambda/a_0 \simeq 0{\cdot}363$, $\varphi = 28\,^{\circ}$, $32\,^{\circ}$ as the best. Here, φ is defined as the angle between the $(1\bar{1}0)$ axis and the normal to the scattering plane. Fig. 1 depicts the locations of the possible reflections occuring parasitic to the 222 reflection about this region, compared with an actual azimuthal scan of that reflection in germanium.

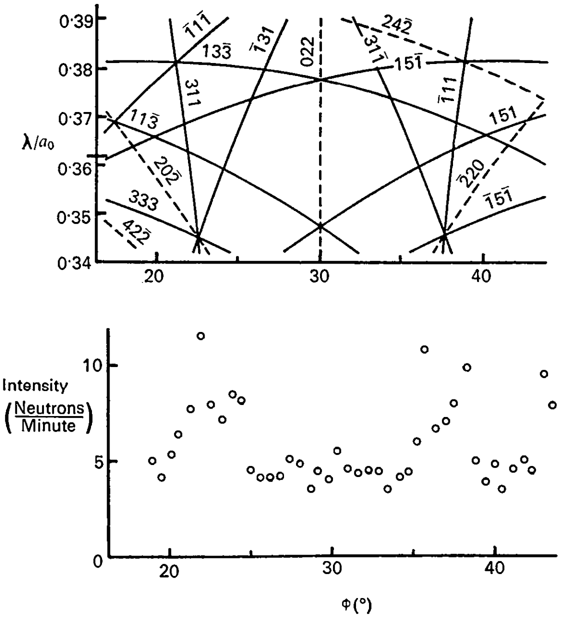

Fig. 1. Azimuthal scan of germanium 222 reflection at $\lambda/a_0 = 0{\cdot}362$ compared with calculated positions of simultaneous Bragg reflections.

Higher order reflections were reduced (though not entirely avoided) in two ways. Firstly we used a mosaic silicon monochromator set to the 111 reflection. This greatly reduces second order intensity, while the crystal reflectivity and reactor spectrum reduce higher orders. Less than 2% higher order contamination was observed in the beam thus prepared. Secondly the samples were chosen to be nearly perfect crystals, thus the reflectivity of the allowed reflections was minimized. Though the strong reflections of these crystals demonstrated nearly maximum extinction, the 222 reflection is so weak as to be essentially extinction free (see below); thus we do not sacrifice any possible forbidden intensity through this choice of samples. Filters of gadolinium oxide and samarium sulfate provided a further check on the wavelength (and thus the reflection order) of any intensity observed in the [222] direction.

The samples used were discs of 2·5 to 3·8 cm diameter cut from intrinsic, low dislocation crystals obtained from Texas Instrument Corporation. Samples were oriented, polished and etched such that their flat faces were true (111) crystallographic planes to within six minutes of arc.

Reflectivity measurements were made with the crystals in the symmetrical Bragg configuration. The ideal expressions relating integrated intensity with reflection structure factor for attenuation-free crystals are (Zachariasen, 1967*a*; James, 1965)

$$R^{\text{perfect}}_{\text{crystal}} = \frac{N_c\lambda^2|F_{hkl}|\exp\{-M(T)\}}{\sin 2\theta} \times \tanh\left\{\frac{N_c\lambda|F_{hkl}|\exp\{-M(T)\tau\}}{\sin\theta}\right\} \quad (2)$$

$$R^{\text{mosaic}}_{\text{crystal}} = \frac{N_c^2\lambda^3(F_{hkl}\exp\{-M(T)\})^2\tau}{\sin 2\theta\,.\,\sin\theta} \quad (3)$$

where N_c is the unit cell density of the crystal, θ the Bragg angle, and τ is the thickness of the crystal (0·575 cm and 1·249 cm for silicon and germanium respectively).

The attenuation coefficient of our samples was measured over our temperature range at $\lambda = 2{\cdot}047$ and 1·986 Å for germanium and silicon respectively. We found:

$$\mu_{\mathrm{Ge}} = (1{\cdot}34 \pm 0{\cdot}079) \times 10^{-4} \times T(^{\circ}\mathrm{C}) + (0{\cdot}151 \pm 0{\cdot}004)\ \mathrm{cm}^{-1} \quad (4a)$$

$$\mu_{\mathrm{Si}} = (0{\cdot}308 \pm 0{\cdot}04) \times 10^{-4} \times T(^{\circ}\mathrm{C}) + (0{\cdot}018 \pm 0{\cdot}005)\ \mathrm{cm}^{-1}\,. \quad (4b)$$

Attenuation in these samples is chiefly attributable to inelastic scattering and true nuclear absorption. Since neutron attenuation is low, we include it in the above expressions for integrated reflectivity by setting

$$\frac{\tau}{\sin\theta} \rightarrow \frac{1-\exp\{-2\mu\tau/\sin\theta\}}{2\mu} . \qquad (5)$$

This is only an approximation, but it does yield the correct asymptotic forms of equation (2) when $\mu\tau/\sin\theta$ is small and F_{hkl} is either very large or very small.

The experimental arrangement used is shown in Fig. 2. The incident beam was limited to the face of the crystal sample by a pinhole mask. Rocking curves of the strong 111 reflections were made, and integrated reflectivities determined from these measurements and the previously measured intensity of the incident beam.

Results

In Table 1 we present measured values of the 111 integrated reflectivity of our samples in comparison with values calculated from equations (2) and (3). The uncertainty noted in the measured values arises solely from neutron counting statistics. That cited for the calculated values is due to uncertainties in neutron wavelength, nuclear scattering length [taken to be $0{\cdot}84\times10^{-12}$ and $0{\cdot}416\times10^{-12}$ cm as reported for germanium by Bacon (1962) and for silicon by Shull (1968)] and sample thickness.

Table 1. *Integrated reflectivity of* 111 *reflection of germanium and silicon in units of* 10^{-5} *radians*

	λ	R_{111} observed	R_{111} perfect	R_{111} mosaic
Ge	2·047	$2{\cdot}32\pm0{\cdot}03$	$1{\cdot}83\pm0{\cdot}01$	2180 ± 10
Si	1·986	$0{\cdot}99\pm0{\cdot}01$	$0{\cdot}99\pm0{\cdot}006$	525 ± 4

To further test the perfection of our samples, double crystal rocking curves were made, using the torsion goniometer described by Shull, Billman & Wedgwood (1967). In all of these tests, the silicon results were indistinguishable from predictions of dynamical theory. The germanium, however, consistently demonstrated small departures from these predictions, indicating the presence of a mosaic structure.

Rocking curves of the 222 reflections were taken, and the integrated reflectivity was calculated. One week was spent collecting data at each temperature. Within counting statistics, no first order reflected intensity was

Table 2. *Experimental upper limit values of the neutron* 222 *structure factor of germanium and silicon as a function of temperature*

	T (°C)	R_{222} observed (radians)	$F_{222}e^{-M}$perfect (cm/unit cell)	$F_{222}e^{-M}$mosaic (cm/unit cell)
Si (222)	25	$<5\times10^{-9}$	$<4{\cdot}4\times10^{-15}$	$<4{\cdot}4\times10^{-15}$
	320	$<5\times10^{-9}$	$<4{\cdot}4\times10^{-15}$	$<4{\cdot}4\times10^{-15}$
	505	$<5\times10^{-9}$	$<4{\cdot}4\times10^{-15}$	$<4{\cdot}4\times10^{-15}$
Ge (222)	25	$<5\times10^{-8}$	$<2{\cdot}1\times10^{-15}$	$<1{\cdot}2\times10^{-15}$
	400	$<5\times10^{-8}$	$<2{\cdot}1\times10^{-15}$	$<1{\cdot}2\times10^{-15}$
	500	$<5\times10^{-8}$	$<2{\cdot}1\times10^{-15}$	$<1{\cdot}2\times10^{-15}$

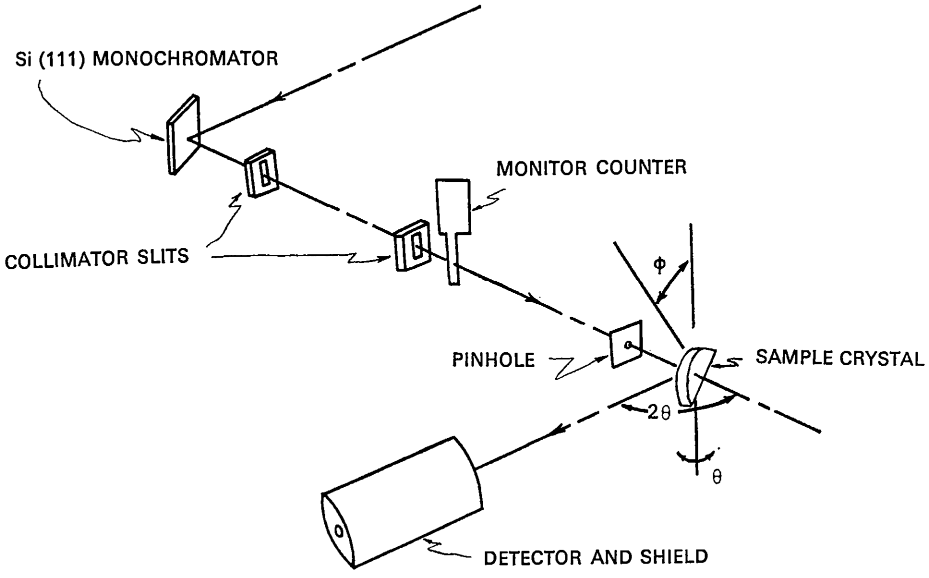

Fig. 2. Experimental arrangement for measurement of single-crystal integrated reflectivity.

observed. Table 2 presents the maximum possible value of the 222 integrated reflectivity consistent with the statistical counting uncertainty involved.

For these experiments, the incident intensity was roughly 10,000 neutrons per second, while the counting rate in the direction of the 222 reflection (background) was of the order of 5 neutrons per minute. The lack of sensitivity evident in the germanium data (indicated by the large possible value of integrated reflectivity) arises solely from additional scatter (inelastic and high order Bragg) which increased the background to a level well above that observed with silicon.

The upper limit values of the structure factore were calculated from the measured integrated reflectivity by means of formulae (2) and (3). For such weak reflections, the results are nearly identical. In the case of germanium, quantitative study of some of the strong reflections, together with an application of Zachariasen's (1967*b*, *c*) treatment of extinction suggests that the 222 reflection is best described by the mosaic crystal solution. Other treatments of extinction, such as that of Weiss (1966), point to the same conclusion.

The largest values of β which could exist consistently with the results of this experiment are $0{\cdot}5\times10^{-11}$ and $0{\cdot}3\times10^{-11}$ erg.Å^{-3} for silicon and germanium respectively. That is, β must be less that one half the value suggested by Dawson & Willis.

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Vibrations des Molécules Formées de Deux Blocs Rigides Simplement Liés

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Schomaker & Trueblood's analysis of the rigid body motion of molecules in terms of three tensors is applicable to some molecules formed by two single bounded parts. If the librations of the two parts round the bond are considered as independent, it is shown that four additional parameters are needed. Then the total number of independent components is twenty-four. This analysis has been applied to eight molecules and a comparison of the two models has been made. For some molecules, the results of the two methods are noticeably different, the analysis permitting independent librations of the two cycles being more satisfactory.

Introduction

Cruickshank (1956) a montré le premier que les vibrations d'ensemble d'une molécule rigide peuvent être déterminées à partir des paramètres d'agitation thermique anisotrope et exprimées au moyen de deux tenseurs symétriques de rang deux: $\mathbf{T}$ (translation) et $\boldsymbol{\omega}$ (libration). Schomaker & Trueblood (1968) ont précisé que dans le cas de molécules non centrosymétriques, un tenseur supplémentaire $\mathbf{S}$, à huit coefficients indépendants, devait être introduit pour tenir compte des corrélations entre translations et librations. Pour