12) correspond to a strong temperature dependence of dc_{ij}/dP. However, as pointed out by these authors, large uncertainties are associated with their results, because they did not perform hydrostatic measurements.

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X-Ray Study of the Debye-Waller Factor of Nb$_3$Sn[†]

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The Debye-Waller (DW) factors for Nb and Sn atoms in the intermetallic compound Nb$_3$Sn have been determined by x-ray intensity measurements on a single crystal. The results are found to be in satisfactory agreement with the theory for both the angular and temperature dependence of the scattering. The data can be fitted by assigning Debye temperatures of 318 °K and 262 °K to the Nb and Sn atoms, respectively. We are unable to confirm the anomalously large value of the DW factor found in a Mössbauer-effect study.

INTRODUCTION

Nb$_3$Sn undergoes a phase transition from cubic to tetragonal symmetry at temperatures below about 50 °K.[1] The elastic constant C_{11}-C_{12}, which represents the stiffness of the shear mode which transforms the crystal from cubic to tetragonal, is found to decrease rapidly as the temperature is lowered, approaching zero at the transformation temperature T_m.[2] Current theories[3,4] attribute the elastic softening to a Jahn-Teller-like mechanism, in which the d-band degeneracy at the Fermi level arising from independent sub-bands associated with the three orthogonal Nb atom chains in the β-W structure, is removed by the tetragonal distortion. In this model the free-energy difference between the cubic and tetragonal states is a function of the strain alone, and the transformation is first order. Since no evidence of a first-order transformation has been observed,[5] the early suggestion that some other order parameter besides the strain might be necessary in the expansion of the free-energy difference near T_m[6] appears compelling. By analogy with certain ferroelectric transitions, the second parameter might be an optical-mode coordinate. In this case, the soft elastic mode appears as a consequence of the interaction of the low-frequency optical mode with the acoustic branch of the phonon spectrum.

Some evidence for such a mechanism was found in a study of the Mössbauer effect in Nb$_3$Sn.[7] It was observed that the recoil-free fraction was anomalously low, corresponding to a Debye temperature of 56 °K at 4.2 °K, and indicative of a large anharmonic contribution to the binding energy. The data could be represented as a combination of a Debye-like spectrum with reasonable $\Theta = 290$ °K, and a temperature-independent opticallike mode, which was interpreted as arising from the loose (square-well) binding of the Sn atoms. (Sn^{119} was the γ-ray source.) However, no evidence of unusual softness in the phonon spectrum has been observed in other measurements (e.g., specific heat,[5,8] and resistivity[4]). Since crystals large enough for neutron scattering studies have not yet been grown, it appeared desirable to check the unusual Mössbauer result by means of x-ray methods. Intensity measurements on single-crystal specimens, in addition to giving the same sort of information as the Mössbauer results, permit the determination of contributions to the diffuse scattering arising from the Nb and Sn atoms separately.

EXPERIMENTAL

An Nb_3Sn single crystal grown by chemical vapor deposition[9] was cut and polished to give parallel $\{100\}$ surfaces about 4 mm^2. In order to study the temperature dependence of the peak intensities the crystal was cemented to the cold stage of a He Dewar with x-ray (Be windows) access, with the [001] direction lying along the goniometer axis of a Siemens Crystalloflex IV diffractometer. Provision was available for independently adjusting the Bragg angle θ (crystal setting), and 2θ (detector setting), so that $(hk0)$ reflections could be observed. In order to compare intensities, as opposed to temperature dependences, it is, in addition, desirable to be able to rotate the crystal about its face-normal so as to maximize the various peak intensities. This was done at room temperature only, by mounting the crystal in a special holder designed for this purpose. In order to guarantee a constant area of irradiation, the crystal was masked by gluing on a 1-mil Au foil with a 2-mm hole centered in the beam.

Mo $K\alpha$ radiation was used in order to observe peaks arising from small d spacings, which are most sensitive to the Debye-Waller (DW) effect. The crystal was irradiated through a very narrow (0.1 mm) slit, while the receiving slit at the detector was made as large as possible (0.6 mm) consistent with reasonable counting procedures. Because of the high intensities available in this technique, counting errors were negligible with respect to systematic errors.

X-ray line intensities are proportional to the square of the structure factor F_{hkl}, which for Nb_3Sn can be written

$$F_{hkl}=2f_{Nb}[\cos 2\pi(\tfrac{1}{4}h)\cos 2\pi(\tfrac{1}{2}l)+\cos 2\pi(\tfrac{1}{4}k)\cos 2\pi(\tfrac{1}{2}h)+\cos 2\pi(\tfrac{1}{4}l)\cos 2\pi(\tfrac{1}{2}k)]+f_{Sn}[1+\cos 2\pi(\tfrac{1}{2}h+\tfrac{1}{2}k+\tfrac{1}{2}l)],$$

where $f=f_0e^{-M}$, f_0 is the atomic scattering factor for an atom at rest, and M is the Debye-Waller factor for the appropriate atom. The DW theory gives for M

$$M=\frac{6h^2T}{mk\Theta_M^2}[\phi(x)+\tfrac{1}{4}x]\frac{\sin^2\theta}{\lambda^2}\equiv 8\pi^2\bar{\mu}_s^2\frac{\sin^2\theta}{\lambda^2}\equiv B\frac{\sin^2\theta}{\lambda^2}, \qquad (1)$$

where h and k are the Planck and Boltzmann constants, m is the atomic mass, $\bar{\mu}_s^2$ is the mean-square displacement in the direction of the reflecting plane normal, and θ and λ are the Bragg angle and x-ray wavelength ($\sin\theta/\lambda=1/2d$). The bracketed term includes the Debye integral

$$\phi(x)=\frac{1}{x}\int_0^x\frac{t\,dt}{e^t-1},$$

where $x=\Theta_M/T$, and the subscript indicates that the Debye temperature appropriate to x rays is slightly different than the thermal Θ because they are calculated by averaging over different moments of the phonon spectrum.[10]

Particularly useful peaks to study are the (14 0 0) and (14 1 0.) These lie in the far back reflection region ($2\theta\sim 140°$) where M is maximal; are of roughly equal intensity; and the closeness of the peaks in both 2θ (0.8°) and interplanar angle (4°) help minimize systematic error. From the structure factor it is seen that the (14 1 0) reflections involve Nb atoms only, while the (14 0 0) is a mixed type, with $F=2f_{Nb}+2f_{Sn}$. Any anomalous DW effects arising from tin atoms should therefore be apparent in a comparison of the two peaks, which are an optimal pair, since there are no pure tin reflections.

RESULTS

The temperature dependence of the (14 0 0) and (14 1 0) reflection intensities is shown in Fig. 1. The data were not extended to below about 50 °K because of the lattice transformation. The linearity of these plots is somewhat unexpected, since theory predicts a saturation of the intensity which should be observable below about 100°K. Front reflection peaks showed a very weak temperature depen-

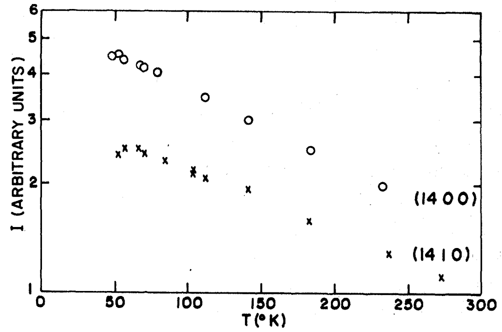

FIG. 1. Integrated intensity as a function of temperature for the (14 0 0) and (14 1 0) reflections.

dence, as expected. However, a small but rapid increase in intensity [10% in the (400) reflection] was observed in the region about 10 °K above the transformation. This is thought to represent a decrease in extinction resulting from a decreasing crystal perfection near the transformation, perhaps connected with critical fluctuations. This effect was not observed in back reflection.

A typical set of room-temperature intensity measurements are summarized in Table I.

Reproducibility of the relative peak intensities under various experimental conditions was about ±6%. This includes the effect of slight misorientations, varying the entrance slit widths, and most importantly, the criteria used for determining the background counting rate. Some additional data taken in the ω-scan mode (fixing the detector at 2θ maximal and rotating the crystal) also fell within this limit.

DISCUSSION

It is convenient to proceed on the assumption that Nb_3Sn is a Debye solid. First we find the appropriate DW factor for Nb. For temperatures near the Debye Θ, it can be shown by expanding the Debye integral[10] that

$$\left[\frac{d\ln I}{dT}\Big/\frac{\sin^2\theta}{\lambda^2}\right]_{T\sim\Theta}\approx 1.90\,\frac{B(\Theta)}{\Theta}\quad .$$

From Eq. (1) and the data of Fig. 1, with $\sin^2\theta/\lambda^2 = 1.76\,\text{Å}^{-2}$ for the (14 1 0) reflection, we find $\Theta_{\mathrm{Nb}} = 318 \pm 15$ °K. The solid line for Nb in Fig. 2 is the theoretical B-vs-T dependence for this Θ. The experimental intensities are converted to B values by using the relation $\ln[I(T)/I(300\,°\mathrm{K})] = 3.52\,[B(300\,°\mathrm{K}) - B(T)]$, where $B(300\,°\mathrm{K})$ is assigned to the curve. It is seen that reasonable agreement is obtained, with a slight positive departure of the data at $T < 100$ °K as mentioned above.

TABLE I. Typical set of counting data for the various reflections of interest. Peaks were scanned over $2\theta_{\max} \pm 0.50°$ at 0.25 °/min, except for the (10 0 0) which was scanned 0.3 ° about $2\theta_{\max}$, in order to eliminate interference from the $K\alpha_2$ peak.

Peak	2θ	Counts	Background	Net intensity
(14 0 0)	139.60	81 590	30 080	51 510
(14 1 0)	140.40	48 260	12 910	35 350
(12 0 0)	107.11	221 400	42 000	179 400
(10 0 0)	84.19	123 500	23 420	100 100

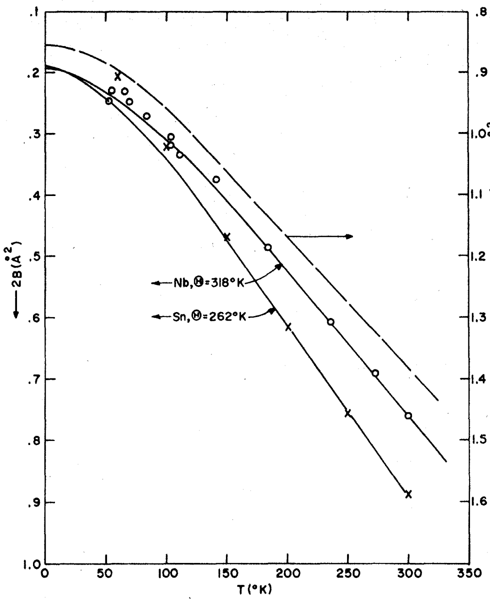

FIG. 2. DW factor $2B$ vs T. Open circles, $2B_{\mathrm{Nb}}$; crosses, $2B_{\mathrm{Sn}}$. The solid lines are the theoretical B-T dependences for the appropriate values of Θ. The dashed line represents the Mössbauer results of Ref. 7. In theory, $2B$ and $1.07\,(-\ln f)$, where f is the recoil-free fraction, should be identical.

For the (14 0 0) reflection, to a very good approximation {all values used in computing intensities—atomic scattering factors, Lorentz-polarization factors, absorption corrections [(14 1 0) only]—were obtained from Ref. 11},

$$\frac{I_{(14\,0\,0)}}{I_{(14\,1\,0)}}\approx\left[\frac{f^{0}_{\mathrm{Nb}}e^{-M_{\mathrm{Nb}}}+f^{0}_{\mathrm{Sn}}e^{-M_{\mathrm{Sn}}}}{2f^{0}_{\mathrm{Nb}}e^{-M_{\mathrm{Nb}}}}\right]^2$$

$$\approx 0.25\left(1+1.6\,e^{-1.76(B_{\mathrm{Sn}}-B_{\mathrm{Nb}})}\right)^2,$$

so that from the I ratios we can compute B for the Sn atoms at various temperatures. These values are given by the crosses of Fig. 2. The data are well fitted over most of the temperature range by a theoretical curve with $\Theta = 262$ °K. In this case, the magnitude of B and its temperature dependence are independently in agreement with theory for the appropriate Θ. The simplest averaging, $\Theta_M = (3\Theta_{\mathrm{Nb}} + \Theta_{\mathrm{Sn}})/4$, gives $\Theta_M = 304$ °K, while from the room temperature elastic constants[2] we get $\Theta_D = 300$ °K.

We conclude that at least above 100 °K, the data are readily interpreted in terms of an ordinary Debye solid. The theory of the Mössbauer effect gives for the recoilless fraction $f = e^{-2B/4\lambda^2}$ so that for the Sn^{119} γ ray, $2B = -1.07\ln f$. We have plotted the smoothed curve of Shier and Taylor as the dashed line of Fig. 2. Note that the ordinate is displaced by 0.7 units in order to bring the curve close to the DW results.

One possibility which remains unresolved is that while $B_{\mathrm{Sn}} - B_{\mathrm{Nb}}$ does not appear to be anomalous,

TABLE II. Theoretical and experimental intensity ratios for three (h00) reflections. The experimental uncertainty is taken to be 6%, and the uncertainty in the calculated ratios computed on the basis of a maximum error of 10% in B_{Nb} and B_{Sn} obtained from the data of Fig. 1.

Peaks	Measured I ratio	Calculated I ratio
(14 0 0)/(12 0 0)	0.287 ± 0.017	0.30 ± 0.02
(14 0 0)/(10 0 0)	0.515 ± 0.031	0.56 ± 0.03
(12 0 0)/(10 0 0)	1.79 ± 0.11	1.86 ± 0.04

the large temperature-independent contribution to f seen in the Mössbauer study represents a motion of the lattice as a whole, i.e., the absolute values of both B_{Nb} and B_{Sn} are larger by an amount $B_0 \sim 0.6$. In this case, a factor $e^{-2B_0(1/2d)^2}$ can be taken out of the intensity formulas, giving rise to an angular-dependent correction to the peak ratios. For $I_{(14\,0\,0)}/I_{(10\,0\,0)}$ this amounts to $e^{-1.72B_0}$, a factor of nearly 2 in the intensity ratio. Table II gives the calculated and measured intensity ratios for the three (h00) reflections studied. The room-temperature values of B from Fig. 2 were used in the calculation. The errors in the calculated values are based on the assumption of 10% errors in B_{Nb} and B_{Sn}.

The agreement is quite satisfactory, and speaks strongly against any anomaly. For the (14 0 0)/(10 0 0) ratio the experimental value lies somewhat too low to be fitted within the estimated experimental error alone. A best fit to all the data, to within a few percent can be obtained simply by increasing B_{Sn} by about 12%, and leaving B_{Nb} virtually unchanged. However, the intensity appears to be increasingly too low as we proceed toward higher index reflections, which suggests the possibility of a systematic error, and the desirability of comparing only nearest-neighbor reflections. We note that the direction of this error is opposite to that which would result from the presence of any additional B_0 contribution to the DW factors.

CONCLUSIONS

Nb_3Sn appears to be an ordinary well-behaved Debye solid. It is noteworthy that even at temperatures close to that of the lattice transformation, where C_{11}-C_{12} vanishes, no anomalous reduction of peak intensities attributable to the lattice softness is observed. This is in agreement with the conclusion from specific-heat measurements[5,8] that the softening is confined to low-frequency phonons. Since the calculation of the DW factor involves an average over a lower moment of the frequency spectrum, i.e., gives more weight to low-frequency phonons, this result is the more striking. Of particular interest is the fact that the same moment is used in calculating the electron-phonon interaction, thereby lending credibility to calculations of the superconducting transition temperature for the β-W compounds[12] based on the usual assumption of a Debye solid.

We are unable to account for the discrepancy between the present work and the earlier Mössbauer study. The difference in DW factor lies well outside the combined experimental uncertainty, particularly at low temperatures. The determination of the *absolute* recoil-free fraction is difficult, as is the determination of an absolute B from x-ray intensities. It is gratifying that at least the temperature dependences appear to be the same for the two sets of data.

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