Anharmonicity and the low-temperature phase in lithium metal

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Neutron diffraction experiments have been carried out on high-purity [7]Li at various temperatures between 4.2 and 300 K. Certain features of the diffraction data indicate that the low-temperature structure is more complicated than simple hcp. The Debye-Waller factor has also been measured using the incoherent elastic scattering by [7]Li and large anharmonic contributions at all temperatures have been found.

I. INTRODUCTION

It has been known since the early x-ray-diffraction work of Barrett and Trautz[1] that body-centered-cubic (bcc) lithium undergoes a structural phase transformation near 70 K. The low-temperature phase was thought to be hexagonal-close-packed (hcp). Because lithium is considered to be a prototypical free-electron metal, having a nearly spherical Fermi surface which lies well inside the first Brillouin zone, there appears to us to be considerable motivation to better understand the nature of this transformation and the low-temperature phase.

We have carried out a series of neutron diffraction experiments on high-purity, polycrystalline [7]Li at various temperatures between 4.2 and 300 K. At low temperatures we have found certain features of the diffraction data which indicate that the structure must be more complicated than simple hcp. In addition, we have found a large, angular-dependent elastic scattering which is due to the influence of the Deybe-Waller effect on the incoherent scattering by the [7]Li nucleus. The importance of a quartic term in the interatomic potential, giving rise to large anharmonic effects in the lattice vibrations, is clearly observed.

II. EXPERIMENTAL

A. Sample and Apparatus

A cylindrical sample having approximate dimensions 1 cm diameter $\times$ 4 cm length was cut from a large polycrystalline ingot of 99.99%-pure [7]Li. Natural lithium contains 7.4-at.% [6]Li, which has a very large neutron absorption cross section. (σ_a = 945 b at a neutron wavelength λ = 1.06 Å.) Consequently, we have chosen to carry out these experiments on the pure isotope. The sample was chemically cleaned and etched, encapsulated in a thin-walled aluminum container, and then mounted in a variable-temperature liquid-helium cryostat. The neutron-diffraction experiments were carried out using the triple-axis spectrometer $3 \times E$ at the University of Missouri Research Reactor.

The Cu(200) monochromator was set to produce an incident beam of nominal wavelength λ = 1.06 Å (energy = 72.8 meV), and the Cu(200) analyzer was oriented to accept only elastically scattered neutrons. The $\lambda/2$ component in the beam, although small, was nevertheless filtered with a [239]Pu filter. The sample was continuously rotated about a vertical axis (normal to the scattering plane).

B. Bragg Peaks

We show in Fig. 1 scans made at three different temperatures, 298, 78 and 4.2 K. In addition to the expected bcc lithium diffraction peaks, several aluminum peaks coming from the sample capsule are observed. As the temperature is lowered from 298 to 78 K the high-angle lithium peaks increase rapidly, indicating a large Debye-Waller effect. Upon lowering the temperature to 4.2 K, a series of new peaks appear. (They first become visible around 60 K.) The lithium bcc peaks decrease in size with the growth of the new peaks, indicating that a new phase has developed at the expense of the bcc phase. On the basis of the decrease of the bcc (310) peak it would appear that approximately 75% of the sample transformed to the new low-temperature phase. The indexing on the 4.2-K scan is based on an hcp phase using Barrett's[2] proposed values for the c and a lattice parameters. fcc indexing is also shown for which we have assumed the same density as for the bcc phase. When this data is carefully plotted on an expanded scale, we find that the location of these peaks and their intensities agree very poorly with the proposed hcp structure.

We cannot be too surprised that the intensity predictions are not in precise agreement with experiment, since it is difficult to prepare a good, random, small-grained polycrystalline lithium sample, even at room temperature. We know that there is preferred orientation in the sample since the counting rate fluctuates rapidly as the sample is rotated (with 2θ fixed on a Bragg reflection).
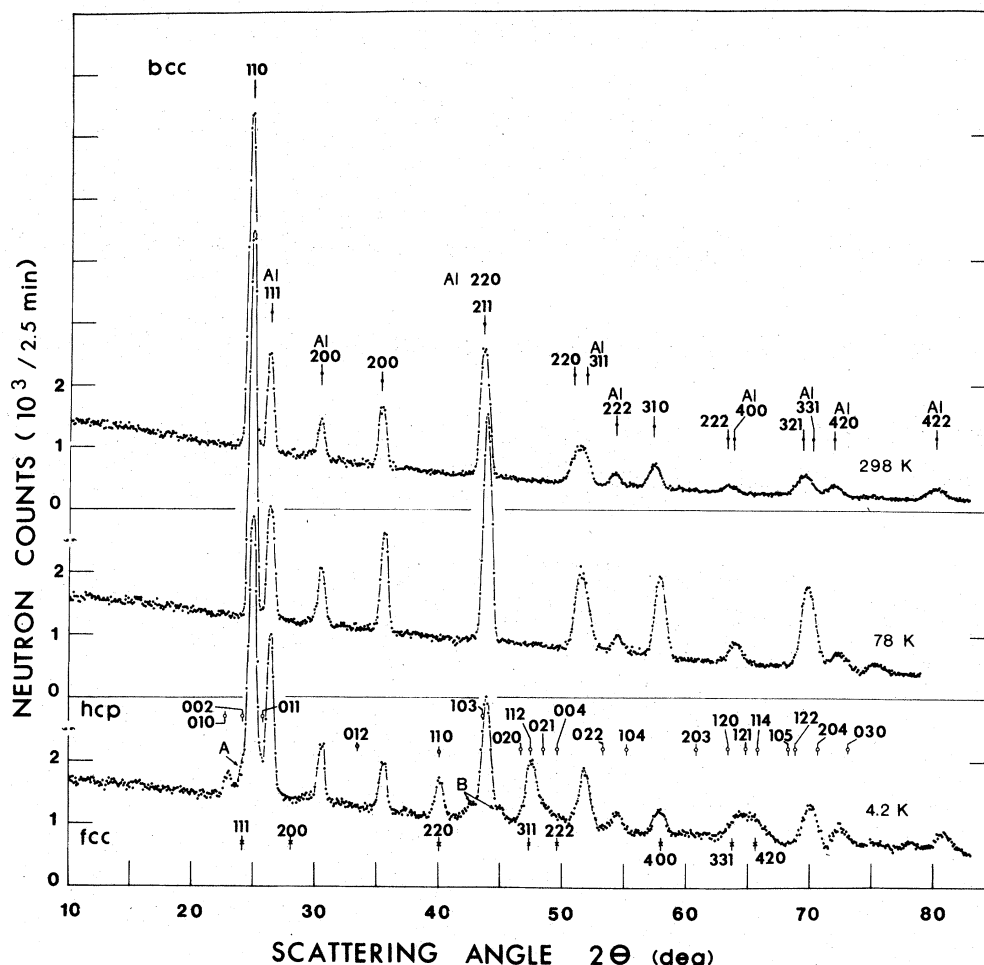
FIG. 1. Neutron diffraction data on polycrystalline ^{7}Li taken on a triple-axis spectrometer at three temperatures. The labeling on the 4.2-K scan for an hcp structure uses the lattice parameters $a = 3.111$ Å and $c = 5.093$ Å. The bcc lattice parameters are $a = 3.502, 3.481$, and 3.480 Å, at $T = 298$, 78, and 4.2 K, respectively.

The integrated intensities of the bcc-Bragg reflections at room temperature, when corrected for the Debye-Waller effect (see Sec. IIC below), indicate that preferred orientation causes variations of order 30% from the predicted structure factors. If one is committed to believing that the low-temperature phase is hcp, then the first new peak appearing in the 4.2-K scan must be labeled (010). On the basis of the estimate of 75% of the sample transforming, we find that this hcp(010) peak is weaker than predicted by a factor of about 8, far beyond the variation expected from preferred orientation. We have replotted the data in the angular range of 20 to 30 degrees in Fig. 2(a). We have subtracted out the aluminum (111) peak from the data by using the 78-K scan. We note that there is a small shoulder (labeled A) on the left side of the bcc (110) peak. This shoulder grows as a function of time as shown by the data in Fig.

2(b) taken approximately 24 hours after the scan a. This feature could be identified as the hcp(002) peak. However, the peak at 26.5° is quite far from the predicted position of the hcp(011) peak. There are additional features of the data which are exceedingly difficult to interpret in terms of a low-temperature hcp phase. Broad "tails," labeled B in Fig. 1, develop on the sides of the (210) bcc peak. These tails increase with time over a period of several hours, if the sample is kept at 4.2 K. The tail on the low-angle side might be interpreted as due to the hcp(103) peak, but the tail on the high-angle side does not correspond to any hcp peak. There are other hcp peaks which are predicted to occur, such as the (012), but do not show up in the data. It would be tempting to interpret the feature B as Huang scattering resulting from the strain induced in the sample by the phase transformation and the coexistence of two phases.
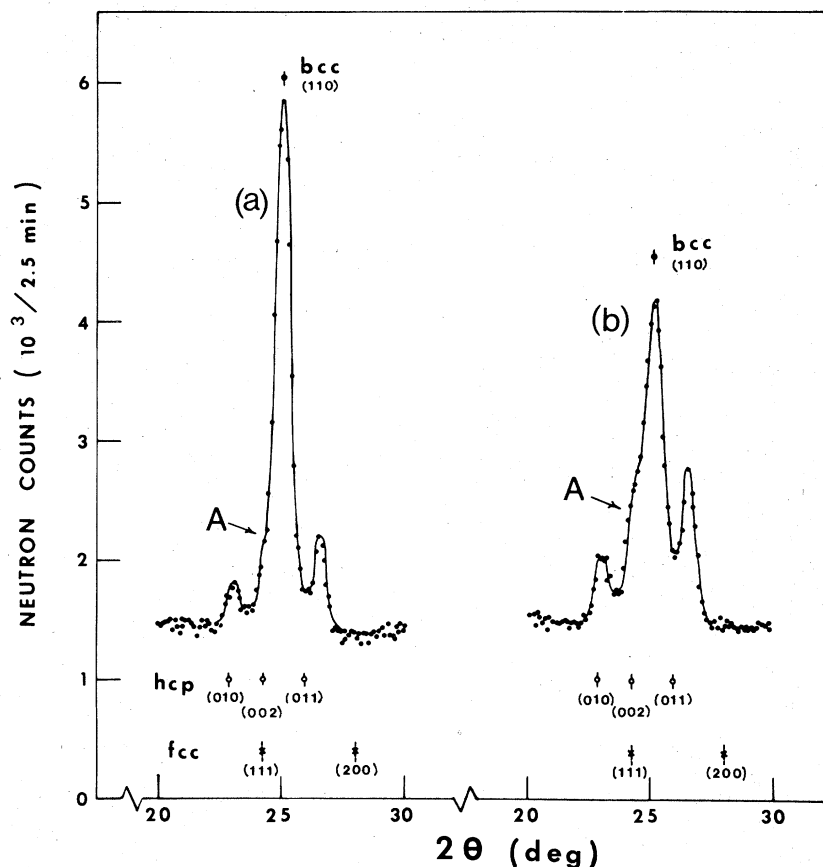
FIG. 2. Expanded scale plot of a scan in the region of the bcc (110) peak showing the development of the feature A in Fig. 1 into a new peak as a function of time at 4.2 K. The data in (b) were taken after keeping the sample at low temperatures for about 24 h. The data of (a) are the same as in Fig. 1.

However, the angular range over which this intensity extends is extremely large.

C. Incoherent Scattering Debye-Waller Effect

The large "background" scattering is due to the incoherent scattering cross section of ^{7}Li ($\sigma_{inc} = 0.62$ b).[3] The sample independent background is negligible (10^{-3}) in these experiments. The angular dependence of this scattering is due to the Debye-Waller factor. Although this scattering is troublesome in accurately measuring the high-angle Bragg peaks, it provides us with an unusual opportunity to determine the Debye-Waller factor, independent of the usual problems of extinction in single-crystal Bragg reflection measurements, and the problems associated with preferred orientation in polycrystals.

In Fig. 3 we have plotted the intensity of the incoherent scattering on a logarithmic scale as a function of the square of the scattering vector $\vec{Q}$ for three temperatures, 298, 78 and 4.2 K. For strictly harmonic motion, these plots would be linear since the Debye-Waller factor is given by

$$e^{-2W_H} = e^{-\langle (\vec{Q} \cdot \vec{U})^2 \rangle} \tag{1}$$

in the harmonic approximation. That is, $2W_H$ is proportional to the mean-square amplitude of vibration $\langle U_Q^2 \rangle$ along the scattering vector within the framework of this approximation. It is clear that there is considerable curvature in these data, especially at the higher temperatures, indicating large anharmonic effects. For a monatomic cubic crystal the leading anharmonic term in the Debye-Waller factor can be shown to be[4]

$$2W_A = -\tfrac{1}{12}[\langle (\vec{Q} \cdot \vec{U})^4 \rangle - 3\langle (\vec{Q} \cdot \vec{U})^2 \rangle^2]. \tag{2}$$

This contribution to the Debye-Waller factor is due to the quartic term in the interatomic potential. In general, it is difficult to evaluate $2W_A$ based on first-principles calculations. However, it can be shown[5] on the basis of symmetry arguments that $2W_A$ can be written as the sum of an isotropic term $2W_A^I$ and an anisotropic term $2W_A^A$ which are of the form
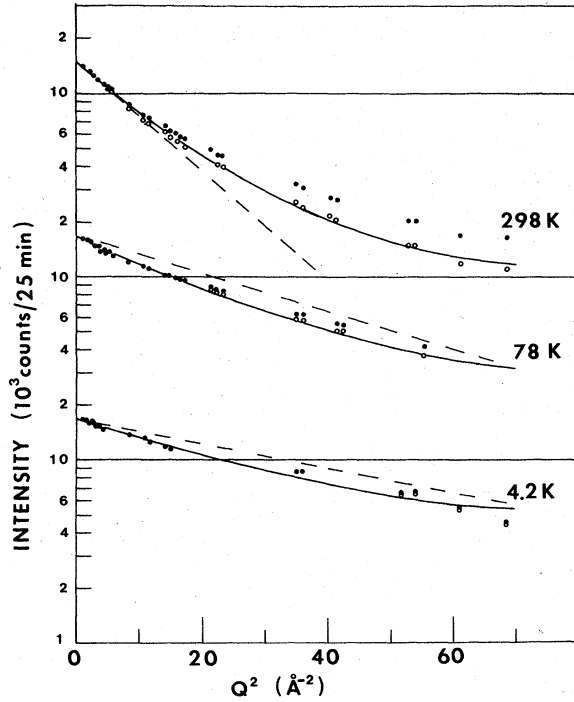
FIG. 3. Incoherent "background" data at three temperatures. The solid circles are the raw data, and the open circles are the data corrected for inelastic scattering. The solid lines are a fit to the data using the form of the Debye-Waller factor given in Eq. (5), and the values of the parameters C and D shown in Fig. 7. The dashed curves are the harmonic approximation Debye-Waller factors calculated from the phonon density of states given by Smith et al. (Ref. 7) as a result of their 78 K phonon dispersion relation measurements.

$$2W_A^A = F(T)[Q_x^2 Q_y^2 + Q_y^2 Q_z^2 + Q_x^2 Q_z^2 - \tfrac{1}{3}(Q_x^4 + Q_y^4 + Q_z^4)]$$

$$(3)$$

and

$$2W_A^I = D(T)Q^4 .$$

$$(4)$$

For our measurements on polycrystalline lithium we are not sensitive to the anisotropic part. We have therefore analyzed our data assuming that the Debye-Waller factor is of the form

$$e^{-2W} = \exp[C(T)Q^2 - D(T)Q^4] .$$

$$(5)$$

A plot of Q^{-2} ln (Intensity) vs Q^2 at a given temperature T should therefore be linear.

It is necessary to correct the raw data of Fig. 3 for the contributions of inelastic incoherent scattering. Even though these experiments were done with a triple-axis spectrometer, the resolution ellipsoid is sufficiently large so as to accept some inelastic scattering. At wave vectors corresponding to 2θ angles between the Bragg peaks the contribution of inelastic coherent scattering to the measured intensity (when the spectrometer is set at $\Delta E = 0$) is essentially zero. Thus, correcting the data for inelastic scattering involves consideration of the incoherent scattering only.

The one-phonon, inelastic, incoherent scattering cross section is given by[6]

$$\left(\frac{d^2\sigma}{d\Omega\, dE}\right)_{\pm} = N\frac{\sigma_{inc}}{4\pi} e^{-2W}\frac{D(\omega)}{\omega}\frac{k}{k_0}\frac{Q^2}{2M}$$

$$\times \left(\langle n\rangle + \tfrac{1}{2} \pm \tfrac{1}{2}\right) .$$

$$(6)$$

Here N is the number of atoms in the sample, M is the atomic mass, k_0 and k are the incident and scattered neutron wavevectors, $D(\omega)$ is the phonon density of states, and $\langle n\rangle$ is the Bose phonon population factor. The + and − signs indicate phonon creation and annihilation. Since we are only interested in very low-energy excitations which fall inside our resolution ellipsoid, we need only consider the quadratic part of $D(\omega)$, namely

$$D(\omega) = A\omega^2 = \frac{3\hbar^3}{(k_B\Theta_D)^3}\omega^2 .$$

$$(7)$$

The Debye temperature Θ_D for lithium is about 325 K. This Debye temperature is appropriate for fitting the quadratic part of $D(\omega)$ as experimentally measured by Smith et al.[7] using coherent inelastic neutron scattering. We take the resolution function be be Gaussian:

$$R(\hbar\omega) = \exp[-(\hbar\omega)^2/2\sigma^2] .$$

$$(8)$$

For these experiments, the width parameter σ was 2.64 meV. Thus, using (6), (7), and (8), we find that the differential inelastic, incoherent scattering cross section averaged over the resolution function is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{inelastic} = \left(\frac{d\sigma}{d\Omega}\right)_{elastic}\left(\frac{12\sin^2\theta_B E_0}{(k_B\Theta_D)^3}\frac{m}{M}\int dx\, \exp(-x^2/2\sigma^2)(e^{|x|/k_B T} - 1)^{-1} + \frac{12\sin^2\theta_B E_0^2}{(k_B\Theta_D)^3}\frac{m}{M}\right) .$$

$$(9)$$

The incident kinetic energy of the neutron is E_0, and θ_B is one half the scattering angle. We have taken the scattering to be nearly elastic in writing Eq. (9), that is

$$Q \approx 2k_0 \sin\theta_B .$$

$$(10)$$

We show in Fig. 4 the ratio of the inelastic cross section to the elastic cross section as a function of temperature. We have used this plot to correct the raw data (dark circles) of Fig. 3 for inelastic incoherent scattering. The corrected data are given by the open circles.
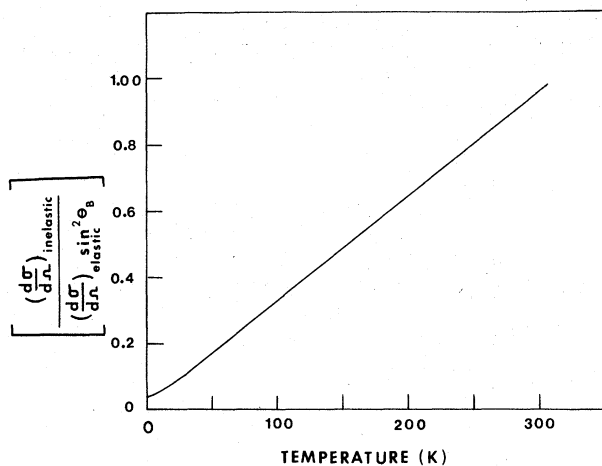
FIG. 4. A plot of the ratio of the inelastic to the elastic incoherent scattering cross sections as a function of temperature for ^{7}Li metal.

To check that this method of correcting the data for inelastic scattering is satisfactory, we have carried out several inelastic scans, one of which is shown in Fig. 5. These data were taken at a scattering vector $Q = 4.2$ Å^{-1} at 280 K. We see that a reasonable extrapolation of the inelastic scattering to frequency $\nu = 0$ agrees with our calculation of the ratio $(d\sigma/d\Omega)_{inelastic}/(d\sigma/d\Omega)_{elastic}$.

In Fig. 6 we show the corrected data at five different temperatures plotted in the form $Q^{-2}\ln(I_0/I)$ vs Q^2 where I_0 is the intensity at $Q = 0$. The intercept on the ordinate gives $C(T)$ and the slope of each of these plots gives the anharmonic coefficient $D(T)$. The series of scans leading to the data shown in Fig. 6 were taken upon increasing the temperature from 4.2 K. We have found that the transformation back to the bcc phase is not complete until about 150 K. These large hysteresis effects were also found by Barrett and Trautz.[1] The temperature dependence of the coefficients C and D are shown in Fig. 7. The effect of the transformation on these coefficients is apparent.
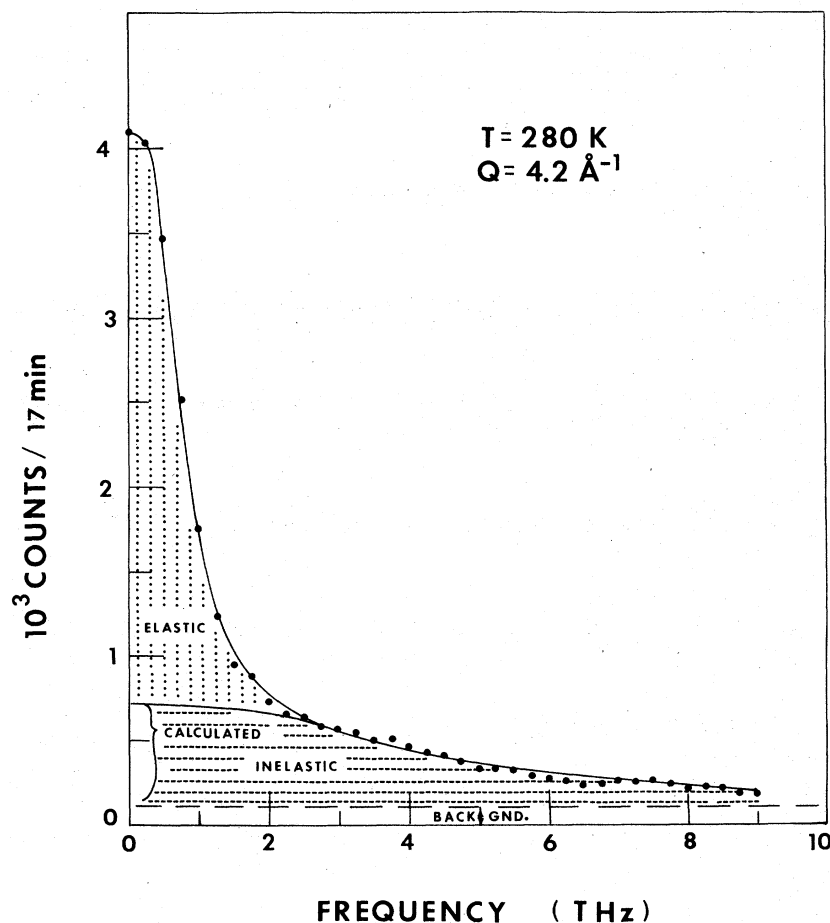
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FIG. 5. A constant Q scan at $Q = 4.2$ Å^{-1} at 280 K.
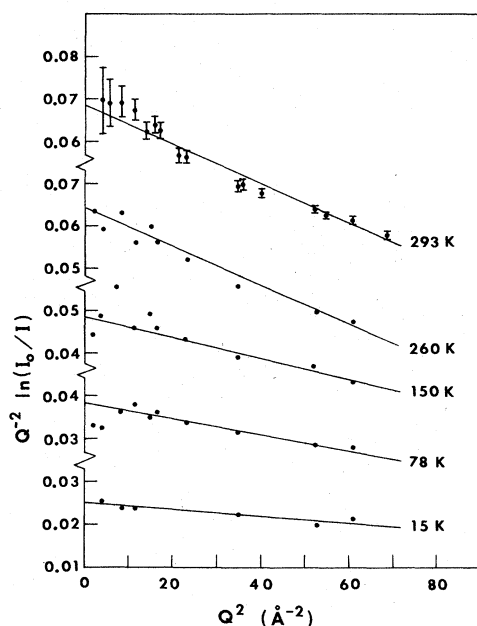
FIG. 6. A replotting of data of the type shown in Fig. 3 in the form $Q^{-2} \ln (I_0/I)$ vs Q^2. According to Eq. (5), plotting the data at each temperature in this manner should yield a linear relationship with an intercept in this manner should yield a linear relationship with an intercept given by the "harmonic" coefficient $C(T)$ and a slope given by the "anharmonic" coefficient $D(T)$.
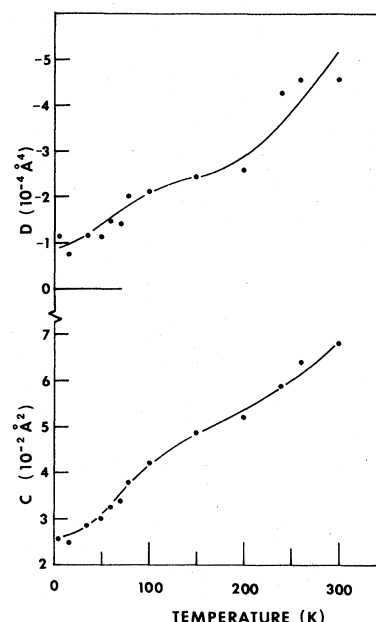
FIG. 7. This figure shows the temperature dependence of the "harmonic" coefficient $C(T)$ and the "anharmonic" coefficient $D(T)$ resulting from analysis of the incoherent scattering data based on plots of the type shown in Fig. 6.

of multiple scattering on the observed angular dependence of the scattering. Multiple incoherent scattering must be negligible since $N\sigma_{inc}R \approx 0.03$ for these experiments ($N \approx 4.6 \times 10^{22}$ atoms/cm³, $R \approx 1$ cm). A multiple-scattering process involving Bragg scattering and then a subsequent Bragg scattering or an incoherent scattering would, in general, lead to increased scattering near $2\theta = 0$. However, an extrapolation of the observed intensity to $2\theta = 0$, resulting in the same value of I_0 at all temperatures requires this to be unimportant also.

III. CONCLUSIONS

It appears to us that it will be exceedingly difficult to determine the actual structure of the low-temperature phase of lithium metal based on only polycrystalline diffraction data. We have tried several alternative explanations for the data shown in Fig. 1 based on an fcc structure in coexistence with the bcc and an hcp phase. So far, these at-

tempts have been unsuccessful. We have recently initiated a project to grow single-crystal samples of ⁷Li. The hope is that when the transformation occurs in a single crystal a limited number of grains of the low-temperature phase will develop, and that we can identify photographically those Bragg peaks due to a specific grain. We believe that it will also be interesting to measure the anisotropic part of the anharmonic Debye-Waller factor, using the incoherent scattering cross section. It seems likely that the large anharmonicity which we have observed in lithium will prove to be an important aspect of the phase transformation. Concrete information on this question can only be obtained reliably from single-crystal experiments.

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