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Temperature-Dependent Isomer Shift and Anharmonic Binding of Sn^{119} in Nb_3Sn from Mössbauer-Effect Measurements*

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We have studied the temperature dependence of the Mössbauer recoil-free fraction and the line shift of Sn^{119} in several Nb_3Sn absorbers between 4 and 375°K. The recoil-free fraction measurements show that the forces on the tin atoms are highly anharmonic. The line-shift measurements are interpreted in terms of a temperature-dependent electron density at the tin nucleus, which is shown to support previous suggestions of a very narrow *d* band near the Fermi level.

I. INTRODUCTION

The intermetallic compound Nb_3Sn and several isomorphous compounds have attracted great attention in recent years because of their high superconducting transition temperatures and critical fields. Recently it has been found that V_3Si and Nb_3Sn have low-temperature phase tarnsitions at ~22°K[1] and ~43°K,[2] respectively, in which the cubic high-temperature β-tungsten (A-15) structure transforms into a tetragonal low-temperature structure. This phase transition is accompanied by a pronounced drop in the elastic stiffness at low temperatures, for shear waves propagating along a [110] direction with $[1\bar{1}0]$ polarization.[3,4] It has been suggested that the phase transition is a second-order one arising from instability of one of the optical phonons.[5]

Study of the Sn^{119} Mössbauer resonance in Nb_3Sn can provide the following kinds of information about the phase transition: (a) If the tin atoms have a noncubic environment below the phase transition temperature, quadrupole splitting of the resonance line would result, (b) the presence of a "soft" phonon mode should be reflected in the temperature dependence of the zero-phonon line intensity, and (c) if the phase transition involves a change in the electronic structure, there may be a change in the isomer shift.

We have studied the Sn^{119} Mössbauer resonance in Nb_3Sn as a function of temperature for several Nb_3Sn absorbers. In none of the samples did we observe line broadening that could be attributed to the appearance of quadrupole splitting due to a departure of the tin site from cubic symmetry, but we did observe a small dip in the Mössbauer recoil-free fraction such as occurs for the phonon instability in a ferroelectric material.[6] Because the amount of lattice distortion that appears below the phase transition temperature is very small in Nb_3Sn,[2] it remains possible that there is quadrupole splitting which is beyond the resolution of our measurements.

The Mössbauer recoil-free fraction is rather low ($\approx$0.45) at low temperatures and has a relatively weak temperature dependence. It can be shown from an inequality derived by Housley and Hess[7] that this behavior is incompatible with the harmonic approximation for the lattice dynamics of this compound, so that anharmonic effects on the Sn^{119} recoil-free fraction must be substantial.

An unexpected feature of the measurements is the large temperature dependence of the line position at temperatures below 100°K. Measurements of the shift in the energy of the Mössbauer line, which arises from the isomer shift and the thermal red shift,[8] indicate an anomalously large temperature variation in the low-temperature region where the thermal red-shift contribution should be negligible. We believe that this arises from a change in the isomer shift with temperature, in which electrons are thermally excited from a narrow *d* band lying at the Fermi level into an *s* band, causing an increase in the *s* electron density at the tin nuclei. The sign of the observed temperature variation indicates that the Fermi level lies near the top of the narrow *d* band, i.e., that the *d* band carriers are holes.

A preliminary account of part of this work has been given.[9]

II. EXPERIMENTAL

A. Experimental Arrangement

The Nb_3Sn samples were used as absorbers. A Mg_2Sn γ-ray source (previously described[9]) was used for some

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of the first measurements, but most of the measurements were done using a Pd_3Sn source, which offers considerable advantages in strength of the resonance and is self-filtering with respect to the nearby unwanted tin K x rays. The source was mounted on the end of a vertical drive rod attached to a transducer on top of the cryostat which provided a triangular-wave velocity modulation. Friction in the drive system was minimized by using a very thin metal bellows where the drive rod entered the vacuum space, and placing a thin flexible metal spider near the bottom of the drive rod to constrain it laterally. The diameter of the bellows was small enough to require but little tension on a spring at the top to overcome the slight displacement of the drive rod whenever the internal pressure was changed. The drive rod was not otherwise in mechanical contact with the cryostat. Calibration runs with an Fe^{57} Mössbauer source indicated that the motion of the source accurately followed that of the transducer. The frequency of the drive was always kept below the lowest transverse vibrational mode frequency of the drive rod (about 40 Hz). A thin window in the bottom of the tube in which the drive rod runs allowed the space to be filled with helium exchange gas to ensure thermal equilibrium with the cryogen bath.

The absorber was mounted on a copper ring $\frac{1}{2}$ in. below the source. This ring was provided with calibrated AuFe-Cu and Cu-Constantan thermocouples for temperature measurement and a heater for temperature regulation. The absorber ring was placed in a vacuum space and was connected to the cryogen bath by a thin-walled inconel tube; the temperature of the ring and attached absorber was regulated by a feedback system that controlled the current in the heater. The absorber temperature could be held constant to within ±0.05°K below 75°K, and the regulation was no worse than ±0.3°K between 75 and 375°K.

Thus the γ rays passed through a 0.0003-in. stainless-steel vacuum window, through the absorber, through a 0.001-in. palladium foil window (critical-edge filter for tin K x rays) and out through a beryllium window in the bottom of the cryostat. Here they were detected with a lithium-drifted silicon detector. The high resolution [<1 keV full width at half-maximum (FWHM)] of this detector enabled us to eliminate nearly all of the remaining tin K x rays. The counts from the detector were registered by a multichannel analyzer operating in time-mode synchronization with the velocity sweep. Each half-cycle of the triangle velocity sweep was stored separately, so every datum is the average of two independent spectra.

B. Absorbers

The three Nb_3Sn absorbers, each containing natural abundance Sn^{119}, were prepared as follows:

(1) Mixed powders of the metals were sintered and subsequently arc melted. The absorber was made by grinding the brittle Nb_3Sn in a mortar and pestle and suspending the powder in epoxy resin. The Nb_3Sn thickness was 20 ± 1 mg/cm^2.

(2) This sample was made by chemical vapor deposition onto a steatite substrate and has a thickness of 17 ± 1 mg/cm^2.

(3) This sample was made with vapor transport grown single-crystal material, which had been subsequently annealed. The material is similar to that used by Mailfert *et al.*[2] The Nb_3Sn was ground and suspended in epoxy resin like sample (1).

C. Treatment of Data

The Mössbauer-resonance spectrum consisted of a single line in all cases. The line was observed to be slightly asymmetric, with the resonant absorption dropping off more rapidly on the high-energy side of the line (when the source was moving toward the absorber). The parameters of the resonance line were determined by using a nonlinear least-squares computer program to fit the data to the function

$$\text{Counts/channel}=A-B\Bigg/\left[1+\left(\frac{x-D}{C}\right)^2\right]+E(x-D)\Bigg/\left[1+\left(\frac{x-D}{C}\right)^2\right]^2 \quad (1)$$

for the spectra in each half of the multichannel analyzer. Here x is the channel number (which is proportional to the source velocity). This function represents a Lorentzian absorption line (first two terms) with asymmetry (the third term). The degree of asymmetry in the absorption line can be specified by the dimensionless asymmetry parameter EC/B, which was found to be 0.7 ± 0.1. This parameter was the same for all samples, all temperatures, and both sources, within experimental error.

The isomer shift was determined from the velocity corresponding to maximum absorption, i.e., the true minimum of function (1) rather than the fitted parameter D, although the trend of the results is not sensitive to this choice. The percent absorption used to determine the recoil-free fraction was likewise taken to be the true maximum absorption rather than the B parameter, and the linewidth was then adjusted to give the same area as the fitted curve (1).

D. Pd_3Sn Source

The Pd_3Sn source used in most of this work was prepared by arc melting the elements. The source was prepared by grinding the brittle arc-melted lump in a mortar and pestle and suspending the powder in a layer of epoxy resin.

To evaluate the source parameters at 19.4°K we took a series of spectra for room-temperature metallic tin absorbers of various thicknesses. The spectra were corrected for background (about 3%) and compared

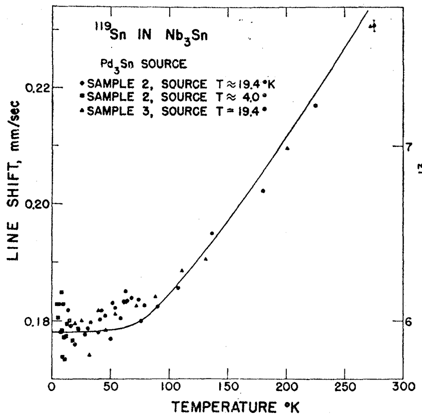

FIG. 1. Line shift as a function of temperature for two samples of Nb$_3$Sn (described in the text) for a Pd$_3$Sn source corrected to 19.4°K. A typical random error is indicated; absolute values of the shift may be different by ±0.02 mm/sec.

to exact spectra generated by a computer, proceeding by trial and error to a "best" set of parameters.

The computer program used the following input parameters, the Pd$_3$Sn source and Sn absorber recoil-free fractions f_S and f_A, the source and absorber linewidths w_S and w_A, the absorber thickness and quadrupole splitting, and the Mössbauer cross section σ_0. Effects due to self-absorption in the source were calculated to be negligible. It was assumed in the calculation that a broadened line can be represented by a Lorentzian function with greater than natural width.

The thicknesses of the absorbers were measured, and the Mössbauer cross section was taken as 1.33×10^{-18} cm^2.[10] The absorber linewidth was taken to be about the natural linewidth, $w_N=0.345$ mm/sec.[11] The remaining parameters for the source at 19.4°K and the absorbers at 298°K were determined to be

$$f_S=0.75\pm0.05,$$

$$f_A=0.050\pm0.005,$$

$$w_S=0.473\pm0.040 \text{ mm/sec},$$

$$\Delta_A=0.23+0.06 \text{ mm/sec}.$$

Because of the method used, it is not practicable to assign precise errors to the parameters, and those given above are simply reasonable estimates. The absorber f and quadrupole splitting Δ_A are in reasonable agreement with data in the literature.[12,13] Because the source linewidth w_S is substantially greater than natural, representing the source energy distribution by a single broadened Lorentzian is probably a poor approximation, but since the cause of the broadening is not known, no alternative appears to be available.

III. LINE SHIFT RESULTS

It is well known that the resonant energies for emission of a γ quantum in the source and absorption of a γ quantum in an unlike absorber are not quite equal. This difference arises from the isomer shift, because of the electrostatic interaction of the nucleus with the surrounding electrons, and the thermal red shift which arises from the nuclear motion.[8] The formulas for these shifts are, respectively,

$$\delta E=\tfrac{1}{5}(Ze^2r^2/\epsilon_0)(\delta r/r)[|\psi(0)|^2_{\text{abs}}-|\psi(0)|^2_{\text{source}}], \quad (2)$$

$$\delta E/E=(v^2_{\text{abs}}-v^2_{\text{source}})/2c^2, \quad (3)$$

where E is the resonant γ-quantum energy, δE is a difference between the resonant γ-quantum energies in the source and absorber, Z is the atomic number of the Mössbauer nucleus, e is the electronic charge, $\delta r/r$ is the fractional change of the nuclear radius r between the nuclear first excited state and the nuclear ground state, $|\psi(0)|^2$ is the square of the electronic wave function at the position of the Mössbauer nucleus, v^2 is the mean square of the thermal velocity of the emitting or absorbing nucleus, and c is the velocity of light. In this paper, the line shifts are given in terms of the Doppler velocity δ necessary to produce resonance, for a Pd$_3$Sn source at 19.4°K.

Our results for the line shift as a function of temperature are shown in Fig. 1 for two Nb$_3$Sn samples. The solid line shown is the expected behavior for the red shift based on a Debye term for the acoustic branches and Einstein terms for the optical branches of the phonon spectrum. No attempt to optimize the fit was made because of the *anharmonic* nature of the material and because the (small) contribution to $|\psi(0)|^2_{\text{abs}}$ due to the change with temperature of the density of Nb$_3$Sn is not readily available. We note, however, that the data in the region 20–80°K rise significantly more rapidly than the $\sim T^4$ dependence shown. The simple anharmonic model proposed by Dash, Johnson, and Visscher[14] will have a similar flat region at low temperatures. Furthermore, an appreciable change in the red shift near 65°K would imply a significant specific heat,[8] and this is not observed experimentally.[15]

Since we have ruled out the red shift in accounting for the temperature dependence of the line shift at low temperatures, it follows that the electron density at the tin nuclei (a density that comes only from the s electrons) must vary appreciably with temperature, since all of the other terms in Eq. (2) are independent of temperature. The changes in the shift are of the order of 0.005 mm/sec, which is to be compared with isomer shifts of 2 or 3 mm/sec observed between, say,

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divalent and tetravalent tin compounds.[10] The change in the s electron density is thus of the order of several thousandths of an electron per atom.

The observed behavior is consistent with the suggestion of Clogston and Jaccarino[16] that there is a very narrow d band located quite near the Fermi level, resulting in a very high density of states at the Fermi level. In the absence of such structure, the fractional change in s electron density is just[9] $\sim(kT/E_f)^2$ (k is the Boltzmann constant, T is the absolute temperature, and E_f is the Fermi energy). This estimate is much less than is observed. If, for example, the d-band density of states decreases sharply just above the Fermi level, at high temperatures thermally excited electrons from the d band will go into bands having appreciable s-state admixture, resulting in a change of s-electron density. The sign of the observed effect implies that the s-electron density at a tin nucleus *decreases* at low temperatures. This means that the high density of states near the Fermi level is due to holes rather than electrons, that is, the Fermi level lies very near the *top* of the narrow d band. Such a band structure has been proposed on independent grounds by Bachner *et al.*[17] It has been shown recently by Cohen, Cody, and Halloran[18] that a model in which the density-of-states changes suddenly near the Fermi energy can account for the properties of Nb_3Sn.

The temperature-dependent isomer shift that we have observed gives support to recent theories of materials having narrow d bands, which have been advanced by Labbé and Friedel[19] and Adler and Brooks.[20] These theories explain such phenomena as the semiconductor-to-metal transition in VO_2 and the cubic-to-tetragonal transition in V_3Si in terms of large changes in the occupation of certain bands.

All models (harmonic or anharmonic) give a red shift proportional to T in the high-temperature limit since $\frac{1}{2}mv^2_{\text{abs}}=\frac{3}{2}kT$, where m is the mass of the absorbing nucleus. The high-temperature slope of the solid line in Fig. 1 corresponds to this limit. For a normal solid the high-T contribution to the isomer shift due to thermal expansion is proportional to T and could account for small differences in slope from the classical limit.

In addition to the arguments presented for the change in $|\psi(0)|^2$, a change in the electron density associated with a structural transformation is possible. X-ray measurements[2] have shown that *some* Nb_3Sn samples undergo a cubic-to-tetragonal phase transformation near ~43°K where $a/c=1.0062\pm0.0001$. Such a distortion should produce some nuclear quadrupole splitting and consequent line broadening of the Mössbauer resonance, but no broadening of significance was observed. It is not known whether our samples exhibit a 43°K phase change; rather, the onset of the anomalous region seems to begin near 80°K. A decrease in the recoil-free fraction below about 85°K, involving an additional sample, mutually supports the presence of an anomaly (see Fig. 2).

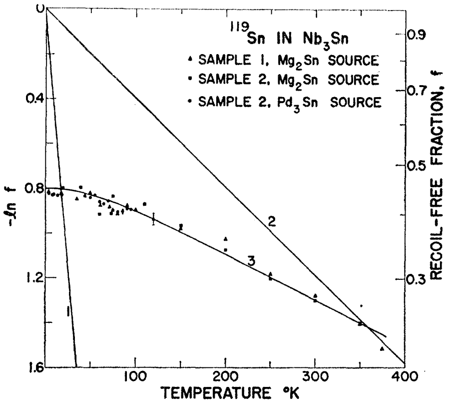

FIG. 2. Absolute recoil-free fraction f as a function of temperature for two Nb_3Sn samples. The limit lines (1 and 2) for the harmonic approximation and the modified Debye curve (3) are discussed in the text. Typical statistical errors for the two sources are shown.

IV. RECOIL-FREE FRACTION

Figure 2 shows the absolute recoil-free fraction f as a function of temperature for samples (1) and (2). The measurements made with the Pd_3Sn source were deemed more accurate (see Sec. II D), and the data[9] using a Mg_2Sn source have been normalized to reflect this change. The resultant f values are about 14% lower, but are substantially higher than those quoted by Delyagin *et al.*[21] Because of the inherent difficulties in determining absolute f values from absorber experiments, the systematic error common to all the points shown might be as much as ±20% of the quoted f values; however, the random error is much less, as shown in Fig. 2.

The recoil-free fraction is rather low, and its temperature dependence is not very strong. This indicates that the mean-square displacement of a tin atom in Nb_3Sn is fairly large and is not very temperature-dependent. Such a situation would occur, for example, for a particle in a highly anharmonic potential well such as a square well. The existence of anharmonic binding can be demonstrated using the following formula which follows from the work of Housley and Hess[7]

$$f(T)\leq\exp\{-(2kT/E_R)[\ln f(0)]^2\}, \qquad (4)$$

where $f(T)$ is the recoil-free fraction at absolute temperature T and E_R is the recoil energy of the Mössbauer photon. This formula is valid in the harmonic approxi-

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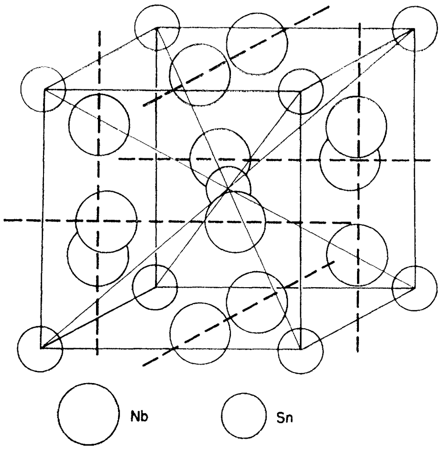

FIG. 3. Structure of Nb_3Sn. The cubic unit cell contains eight atoms, with the tin atoms located in a bcc arrangement and the niobium atoms arranged in three sets of mutually perpendicular chains running along faces of the unit cube. The chains are shown by dashed lines, and have niobium atoms uniformly spaced with half the period of the unit cell.

mation for any frequency spectrum if the Mössbauer nucleus is located at a site with cubic symmetry. The line marked 1 in Fig. 2 shows the upper limit on f given by Eq. (4) using the experimental value $f(0)=0.45$. Alternatively, we can seek a value of $f(0)$ that will give an upper limit that does lie above all of the experimental points. This upper limit is shown by the line marked 2 in Fig. 2, and corresponds to $f(0)=0.79$. In either case, there are large discrepancies with experiment that indicate that the harmonic approximation is not valid for Nb_3Sn.

The structure of Nb_3Sn is shown in Fig. 3. A tin atom sits in an approximately spherical hole surrounded by twelve nearest-neighbor niobium atoms, arranged in three sets of mutually perpendicular chains with spacings half the period of the unit cell. The short distance between the niobium atoms suggests that the bonding between the niobium atoms in the same and adjacent chains is strong, while the evidence discussed above indicates that the forces binding a tin atom are quite weak near its equilibrium position and increase rapidly as it approaches the nearest-neighbor niobium atoms.

An analysis of the recoil-free fraction of an emitting nucleus anharmonically bound to a lattice site has recently been given by Dash, Johnson, and Visscher.[14] They have shown that at high temperatures f is just the product of the f factors that would be calculated for the motion of the lattice as a whole (acoustic modes) and for single-particle motions of the emitting nucleus in its potential well (optical modes), i.e.,

$$\log f=\log f_{\mathrm{ac}}+\log f_{\mathrm{op}}. \tag{5}$$

We expect that f_{ac} is harmonic, while f_{op} is quite anharmonic and only weakly temperature-dependent. Since the high-temperature behavior of a harmonic f must extrapolate to 1 at absolute zero, we can make a crude estimate of f_{op} by extrapolating the high-temperature experimental data to absolute zero.

We can relate f_{op} in a rough way to the radius R of the flat part of the tin potential well using the formula

$$\ln f_{\mathrm{op}}\approx\tfrac{1}{3}(K^2R^2), \tag{6}$$

where K is the wave vector of the emitted photon. This formula is strictly valid only for a harmonic lattice, but if $K^2R^2\lesssim\frac{1}{2}\pi$ as in the present case, the anharmonic corrections to it are small.[22] The data shown in Fig. 2 give, roughly, 0.2 Å for the radius of the flat part of the tin potential well. The values of f_{ac} that follow are shown by the curve marked 3 in Fig. 2 and are consistent with a Debye spectrum for the acoustic modes, with $\Theta=290\pm50°\mathrm{K}$, in rough agreement with specific-heat data.[15]

As mentioned earlier, there is evidence for a small dip in f in the neighborhood of 80°K. This is typical of an unstable optical mode, such as occurs in a ferroelectric,[6] and supports the idea[5] that such a mode might exist in Nb_3Sn type compounds. To date, investigations of the properties of Nb_3Sn have not shown any discontinuous change at the transition above the superconducting critical temperature.

V. CONCLUSIONS

The present study has shown conclusively that the forces binding a tin atom in Nb_3Sn are highly anharmonic. The physical picture of the Nb_3Sn structure arising from this investigation is a rigid framework of niobium chains, loosely enclosing the tin atoms. This suggests that the displacements of the tin atoms in the cubic-to-tetragonal phase transition may be appreciably greater than those of the niobium atoms.

The temperature-dependent isomer shift that occurs in Nb_3Sn may be associated with a very narrow d band, with the Fermi level lying near the top of the band. The isomer-shift measurements imply a change of s-electron density with temperature, and hence provide direct evidence in favor of the pseudo-Jahn–Teller effect proposed[17] to explain the cubic-to-tetragonal structure change in the isomorphous compound V_3Si.

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