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Lattice Softening and Anisotropy at ^{119}Sn Sites in $SnMo_6S_8$†

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The vibrational motion of Sn in the high-critical-field superconductor $SnMo_6S_8$ has been studied with the ^{119}Sn Mössbauer effect. The Mössbauer thermal shift and recoil-free fraction are found to contain large anharmonic contributions from the soft modes. The soft vibrational motion contributes substantially to the mass enhancement λ.

There is considerable current interest in the ternary superconductors based on the molybdenum sulfides. Recent studies indicate superconducting transition temperatures T_c as high as 14.4 K and upper critical fields as high as 600 kG.[1] The third element in the ternaries is clearly of great importance in determining the superconducting properties of these compounds. For example, when the third element is removed by chemical treatment, a slight triclinic deformation takes place and no superconducting transition is detected to less than 1 K.[2] Thus, investigations of the local properties of this component are of importance in understanding these materials. In this regard, $SnMo_6S_8$ provides an interesting case to study. While many of these materials show lattice instabilities with a first-order phase transition, neither crystallographic and resistivity[3] nor heat-capacity and susceptibility[4] measurements show a transition for the Sn-based compounds. In addition, this class of compounds has the largest pressure dependence of T_c yet found for any superconductor.[5] In this Letter we report a Mössbauer study of the lattice properties of ^{119}Sn in $SnMo_6S_8$. The measurements show (1) anisotropic mean-square lattice displacements with $\langle z^2\rangle - \langle x^2\rangle < 0$ and a strong deviation from harmonic behavior; (2) a temperature-dependent line shift indicative of large anharmonicity and soft modes; (3) a possibly large contribution of the soft vibrational modes to the mass enhancement λ, and hence to the high T_c.

Mössbauer spectra were obtained as a function of temperature and external magnetic field on a $SnMo_6S_8$ sample having $T_c = 10.8$ K. X-ray measurements showed a small quantity of α-Mo and the Mössbauer spectra showed ~5% β-Sn present in addition to the rhombohedral (Mo_6Se_8-type) $SnMo_6S_8$. The β-Sn spectra were stripped from the data using the results of Rothberg, Grumard, and Benczer-Koller[6] and Hohenemser.[7] The linewidth of the absorber versus a 15-mCiV(Sn)

source was 0.82 ± 0.02 mm/sec, independent of temperature between 5 and 160 K. The source was thermally clamped to 273.53 ± 0.05 K except for the applied-field measurements where both source and absorber were at 4.2 K.

The high-T_c members of the Mo_6Se_8 structural family, $SnMo_6S_8$ and $PbMo_6S_8$, have been found to retain the rhombohedral $R\bar{3}$ structure to 4.2 K. Crystallographic studies[8] place the third element in channels between units of Mo_6S_8 linking Mo atoms in adjacent units. Marezio *et al.*[9] found that the $PbMo_6S_8$ structure consists of a distorted cubic network of S atoms with every fourth cube occupied by a Pb atom or a Mo_6 octahedron. Because of the axial site symmetry at the Sn, we take the electric-field-gradient asymmetry parameter to be zero. The quadrupolar interaction partially removes the degeneracy of the $\frac{3}{2}$ excited state level and leads to a doublet (π and σ lines) whose intensities in a powder sample are equal in the absence of lattice anisotropy. The anisotropy in the Debye-Waller factor[10] can then be determined from the ratio of intensities $R = I_\pi / I_\sigma$ (the Goldanski-Karyagin effect). For random orientation of particles, these intensities are

$$I_\pi = \exp(-k^2\langle x^2\rangle)\int_0^1 (1+u^2)\,\exp(-\epsilon u^2)\,du \qquad (1)$$

and

$$I_\sigma = \exp(-k^2\langle x^2\rangle)\int_0^1 (\tfrac{5}{3}-u^2)\,\exp(-\epsilon u^2)\,du, \qquad (2)$$

where $u = \cos\theta$, θ is the angle between the principal axis of the electric-field-gradient tensor and the direction of observation, k^2 is the square of the γ-ray wave vector, and $\epsilon = k^2(\langle z^2\rangle - \langle x^2\rangle)$. The zero-field spectrum at 4.2 K where anisotropic effects are a minimum, showed a symmetric quadrupole doublet with a splitting of 0.81 ± 0.01 mm/sec. Spectra obtained in an external field (30 kG) show unequivocally that the quadrupole interaction parameter e^2qQ is positive, which means that the σ line (transitions $\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}$) is lower in energy than the π line (transitions $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$).[11] As the temperature is increased, the π line becomes increasingly more intense than the σ line. This behavior is characteristic of an anisotropic Debye-Waller factor (and not characteristic of preferred particle orientation). In the present case, the data give $R > 1$, which shows that $\epsilon < 0$.

From the temperature dependence of R we have obtaine $\epsilon(T)$. Using these values in Eqs. (1) and (2), we then obtained the temperature dependence of $\langle z^2\rangle$ and $\langle x^2\rangle$, shown in Fig. 1. As one sees, there is a change in slope in the vicinity of 80 K.

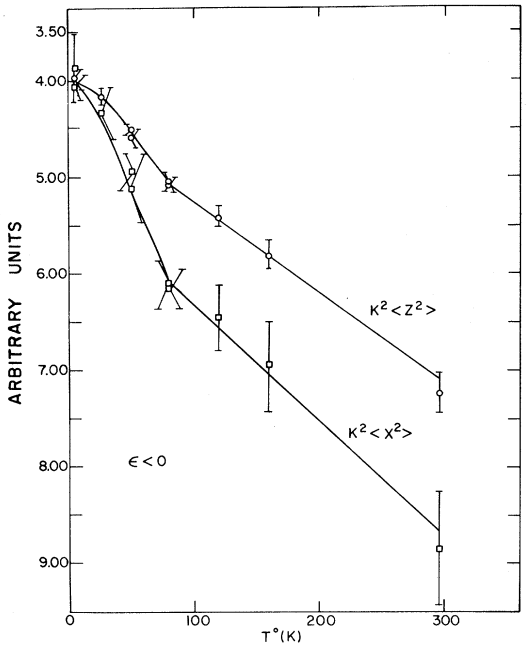

FIG. 1. Temperature dependence of $\langle z^2\rangle$ and $\langle x^2\rangle$. Solid curves are based on Debye models.

To roughly characterize the change, we have fitted Debye models to the temperature regions below and above 80 K; the Debye temperatures are shown in the figure. Note, however, that the relative zero-point displacement would shift the curves from that shown in Fig. 1. In fact, the decreasing absolute value of the slope at high temperatures can be accounted for[12] by anharmonic contributions to the Sn vibrational motion, which can lead to modifications of the relation between the recoil-free fraction and $\exp(-k^2 \times \langle x^2\rangle)$.[13]

The dependence of the line shift δ on temperature (Fig. 2) shows a striking change in the same temperature region. We consider changes arising from the isomer shift δ_{IS} and the thermal shift δ_{TH}. The isomer shift can change due to thermal expansion or interband charge transfer. The temperature dependence of the Debye-Waller factor indicates an increase in volume with increasing temperature. According to measurements[14] of δ_{IS} in β-Sn and Pd(Sn), this should cause a change opposite to the observed temperature dependence of the shift in $SnMo_6S_8$. In the absence of a structural phase transition, isomer-shift changes below 200 K are normally small.[15] The weak temperature dependence of the susceptibility[4] of $SnMo_6S_8$ indicates that there is no

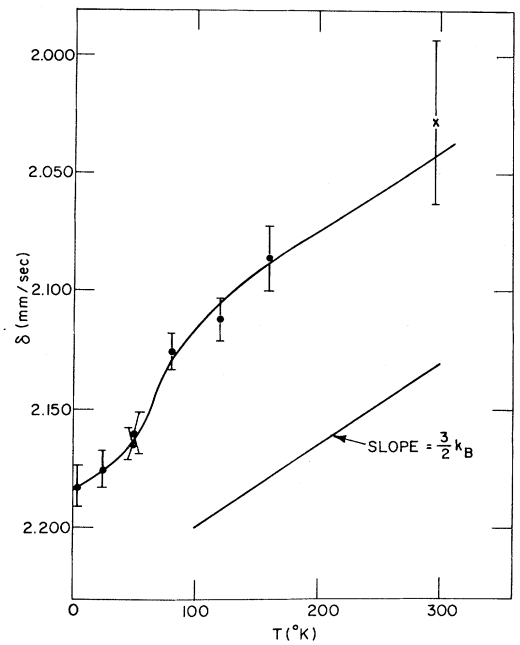

FIG. 2. Shift $\delta(T)$ versus T. The slope between 5 and 25 K is close to that for a Debye curve with $\Theta_D = 40$ K. Only differences in Debye temperature have significance, however. Also shown is a curve for $\delta_{TH}(T)$ in the classical limit when $\langle v^2 \rangle$ approaches $3k_BT/2M$. The shift is quoted relative to the V(Sn) source. The shift of a $BaSnO_3$ absorber relative to this source at 295 K is -1.580 ± 0.004 mm/sec.

sharp structure in the density of states near the Fermi level. Consequently, interband charge transfer and a concomitant isomer-shift variation with temperature should be small. We therefore ascribe the observed temperature dependence predominantly to δ_{TH}.

The thermal shift is proportional to the mean-squared velocity $\langle v^2 \rangle$ of the Sn atom. We note in Fig. 2 that the slope of δ versus T exceeds the classical limit $\frac{3}{2}k_B$ in the region between 25 and 160 K. This cannot be accounted for on the basis of any temperature-independent phonon density of states. In order to characterize the data, we have assumed a quasi-harmonic model. By constructing a family of Debye curves of δ_{TH} versus T with Θ_D as a parameter and placing the data points on these plots, the apparent Debye temperature is found to change from $\Theta_D = 40$ K at $T = 5$ K to $\Theta_D = 640$ K at $T = 160$ K. Such an extreme variation in Θ_D due to the large anharmonicity is indicative of a breakdown in the quasi-harmonic model for $\langle v^2 \rangle$.

The temperature dependence of $\langle v^2 \rangle$ is clearly outside the realm of low-order perturbation treatments of harmonic lattice theory. However, the entropy has been shown to be given by the harmonic expression in infinite-order perturbation theory.[16] Recent heat-capacity results[4] on $SnMo_6S_8$ indicate that the entropy Debye temperature varies from $\lesssim 200$ K near T_c to over 400 K at room temperature. Although the entropy averages over all the lattice vibrations rather than those associated with only the Sn motion, this still indicates an enormous deviation from Debye behavior. In addition, we may note that within harmonic theory,[17] the moments of the phonon spectrum $\omega(n) = [\sum_i \omega_i^n]^{1/n}$ must be monotonically increasing with n. However, for $SnMo_6S_8$ at low temperatures, the moment $\omega(1)$ (obtained from δ_{TH}) is smaller than $\omega(-1)$ (obtained from the mean-squared displacements), again showing the lack of harmonic behavior.

We now consider the implications of the soft modes observed here for the superconductivity of $SnMo_6S_8$. The difference between the superconducting transition temperatures of $SnMo_6S_8$ ($T_c \simeq 11$ K) and the isomorphic binary compound Mo_6Se_8 ($T_c \simeq 6$ K) could be due in large part to the additional soft lattice modes associated with the Sn in $SnMo_6S_8$. That is, an additional contribution to $F(\omega)$ [and presumably $\alpha^2(\omega)F(\omega)$] of weight $\sim 3N_{Sn}$ and energy ω, $40\ \text{K} \lesssim \omega \lesssim 100$ K, would be expected to make a significant contribution to λ.

Previous Mössbauer studies by Shier and Taylor[18] on the high-T_c superconductor Nb_3Sn showed an anomalous change in shift near the temperature of the martensitic phase transition, which they attributed to changes in isomer shift due to interband charge transfer. We note that some of the shift observed in Nb_3Sn may also be due to vibrational softening. Kimball, Weber, and Fradin[19] have also found deviations from Debye behavior of the shift in Ga-rich $V_3Ga_{1-x}Sn_x$ compounds, which were accounted for on the basis of lattice softening at low temperature. We emphasize that the behavior found for the shift in $SnMo_6S_8$ is well outside of the description of harmonic theory, whereas the shift results in Nb_3Sn and $V_3Ga_{1-x}Sn_x$ can be described by perturbation corrections to harmonic theory. The deviations in $SnMo_6S_8$ are so severe that inclusion of anharmonicity as a perturbation to a harmonic model will not be valid.

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Critical Properties of Spin-Glasses*

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The critical properties of the model of a spin-glass proposed by Edwards and Anderson are studied using the renormalization group. The critical exponents are calculated in $6-\epsilon$ spatial dimensions. It is argued that a tricritical point can exist where the nonordering field is the skewness of the distribution of J.

Although spin-glasses, such as dilute solutions of Mn in Cu,[1,2] have been studied experimentally for many years, only recently have formulations been given in terms of a microscopic Hamiltonian.[3-6] Even so, the spin-glass transition has not been successfully related to the usual picture of phase transitions as we shall do here. As in Refs. 3–6 we consider the spin Hamiltonian, $\mathcal{H}$, given by

$$\mathcal{H}/kT = -\sum_{\vec{r},\vec{r}'} K(\vec{r},\vec{r}')\vec{S}(\vec{r})\cdot\vec{S}(\vec{r}'), \tag{1}$$

where $\vec{S}(\vec{r}) = S_1(\vec{r}), S_2(\vec{r}), \ldots, S_m(\vec{r})$ is a classical m-component spin of unit magnitude at the lattice point $\vec{r}$, and $K(\vec{r},\vec{r}') = J(\vec{r},\vec{r}')/kT$, where $J(\vec{r},\vec{r}')$ is a random variable with a probability distribution $P(\vec{r},\vec{r}';J)$, and $J(\vec{r},\vec{r}')$ is assumed to be a finite-ranged interaction. We treat a quenched random system where the average free energy is calculated as the average, denoted $[\,]_{\rm av}$, over all configurations of $J(\vec{r},\vec{r}')$:

$$F = [F(\{J\})]_{\rm av}. \tag{2}$$

According to mean-field theory one expects a ferromagnetic or antiferromagnetic state if $[J(\vec{r},\vec{r}')]_{\rm av}$ is sufficiently large in magnitude. If $[J(\vec{r},\vec{r}')]_{\rm av}$ is zero, Edwards and Anderson (EA)[3] argue that there will still be a transition at a freezing temperature T_f to an ordered state characterized by a new order parameter,

$$q(\vec{r}) = [\langle\vec{S}(\vec{r})\rangle_{\{J\}}\cdot\langle\vec{S}(\vec{r})\rangle_{\{J\}}]_{\rm av}, \tag{3}$$

where $\langle\vec{S}(\vec{r})\rangle_{\{J\}}$ is the thermal average of $\vec{S}(\vec{r})$ for a given configuration $\{J\}$. Note that q is by definition a positive quantity. This will be important in what follows. EA calculate the properties of this spin-glass phase transition using mean-field theory and a Gaussian random distribution of J's centered about $[J(\vec{r},\vec{r}')]_{\rm av} = 0$. They find a continuous transition with an order-parameter exponent of $\beta = 1$ and a finite discontinuity in the slope of the specific heat, $dC(T)/dT$, at $T = T_f$, so that $\alpha = -1$. Similar results were found by other more detailed calculations.[4-6] A straightforward generalization of the EA treatment to in-