FINITE TEMPERATURE LATTICE SOFTENING IN CeSn₃

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Results of temperature dependent Mössbauer effect measurements on Sn in CeSn₃ and LaSn₃ are presented. An anomalous increase in the Sn mean squared displacement (MSD) in CeSn₃ in the 50K region surrounding 135K has been observed. A phenomenological model is developed which relates the results to previous measurements on CeSn₃. This model discusses lattice softening effects near continuous, isomorphic phase transitions such as occur in a number of rare earth compounds.

Introduction

The large difference in ionic volume between the 4fn and 4fn-1 configurations of rare earth elements mandates a strong electro-elastic coupling in rare earth materials near a configurational instability. Recognition of this fact has motivated a number of experimental and theoretical studies. The most profound and elastic anomalies in this field have been observed near the isostructural transitions in the Sm₁₋ₓYₓSi₄₋₁ and Ce₁₋ₓThₓ systems. In the Sm compound velocity of sound, Raman scattering, inelastic neutron scattering, and Debye-Waller factor measurements have indicated an anomalous increase in the local Sm atom volume deformability and in the volume sensitive longitudinal phonon modes. Near the critical point (CP) in the Ce based system divergent behavior in the bulk compressibility and thermal expansion coefficients have been observed.

In this paper we present the first use of Mössbauer spectroscopy (MS) to probe anomalous lattice vibrations in a material, CeSn₃, which has such an electronic instability. Our results motivate development of a phenomenological theory which addresses the coupling of lattice and electronic properties near this and similar isostructural transitions.

Experimental

MS is sensitive to lattice vibrations in the same way as is true for x-ray diffraction intensities. In the thin absorber approximation the integrated area under a Mössbauer resonance is proportional to the exponential of the Debye-Waller factor:

\[ A = A₀e^{-\frac{E_γ^2}{2U²}} \]

Here \( <U²> \) is the MSD of the Mössbauer nucleus (Sn in this study) and \( E_γ \) is the energy of the \( γ \)-radiation (23.871 keV in this study).

The samples were prepared and characterized using standard methods described elsewhere. Details of the \( ^{119}Sn \) Mössbauer effect measurements and temperature dependent data analysis have been previously discussed.

CeSn₃ Background

The compound CeSn₃ has the AuCu₃ structure. Above about 220K this compound appears to be similar to \( γ \)-Ce in terms of both magnetic properties (local moment, Curie-Weiss susceptibility) and effective Ce volume (an estimated valence of about 3.1⁺). Below 200K this system undergoes a non-linear, but continuous, crossover to a lower volume Pauli paramagnetic state. The greatest activity in this crossover is centered between 125-150K where the thermal expansion coefficient and magnetic susceptibility show broad peaks and where the bulk modulus shows an anomalous minimum. Although this behavior is reminiscent of the crossover from \( γ \)-Ce to \( α \)-Ce, in CeSn₃ the change is small (ie. 1% volume change) and continuous.
as opposed to the 12% jump in volume at the first order \( \gamma \rightarrow \alpha \) transition in Ce.

**Results**

We have performed MS on CeSn\(_3\) (and for comparison on LaSn\(_3\)) over the temperature range 78K<\(T<300\)K. Figure 1 shows the logarithm of the integrated area of the Mössbauer resonance, \( \ln A \), versus temperature for CeSn\(_3\) and LaSn\(_3\). The two curves are normalized to the data points at 100K. Using (1) we define the normalized Sn atom MSD, \( <u^2(T)> \)

\[
<u^2(T)> = \frac{\langle \Delta A(T) \rangle}{B} = \ln \left( \frac{A(T)}{A(100)} \right) + <u^2(100)>.
\]  

In ascending order of interest the reader should note that: 1) as is customary, \( <u^2> \) decreases with decreasing temperature for both compounds; 2) \( <u^2> \) for both compounds shows an overall curvature which is presumed to arise from motional anharmonicity and which has been observed in the Mössbauer spectra of a number of compounds\(^2\); and 3) relative to LaSn\(_3\), \( <u^2> \) for CeSn\(_3\) shows a small but well resolved increase (in \( \Delta A \) shows a decrease) near 135 K.

In order to see the anomaly in CeSn\(_3\) more clearly the LaSn\(_3\) results in Fig.1 have been fitted to a quadratic form and subtracted from the CeSn\(_3\) results. This difference is used to define

\[
\Delta<u^2(T)> = <u^2(T)>_{\text{CeSn}_3} - <u^2(T)>_{\text{LaSn}_3} = \ln \left( \frac{A(T)}{A(100)} \right)_{\text{CeSn}_3} - \ln \left( \frac{A(T)}{A(100)} \right)_{\text{LaSn}_3} - C
\]  

In Fig.2 we plot \( \Delta<u^2> \) versus temperature. (The constant \( C \) has been adjusted so that \( \Delta<u^2> \) goes to zero at room temperature).

This anomalous part of the vibrational amplitude, \( \Delta<u^2> \) closely mimics previous thermal expansion coefficient and 20,21 bulk modulus\(^2\) results both in the position of the peak near 135K and in the asymmetric shape of the anomaly (with a broad high temperature rise and a more rapid low temperature cutoff). At its peak value \( \sqrt{<u^2>} \) is about 0.02\( \AA \), comparable to the total thermal dilation of CeSn\(_3\) between 4.2K and 300K. In the Sm\(_7\)Y\(_3\)S system the observed increase in the root MSD of the sulfur atoms (about 0.06 \( \AA \)) is also comparable to the integrated thermal expansion (about 0.05 \( \AA \))\(^2\).

**Ce Volume Fluctuation Coupling to Sn MSD**

To understand the behavior of CeSn\(_3\) one can proceed in analogy to the Sm\(_7\)La\(_3\)S system where it has been shown that local Sm volume fluctuations cause a large displacement of their nearest neighbor (nn) S atoms.\(^2\) Neglecting (for simplicity) higher multipole Ce deformations\(^6\) it is assumed here that in the CeSn\(_3\) matrix, a Sn atom suffers a displacement \( \delta u \) when one of its nn Ce atoms (labeled \( j \)) undergoes a volume fluctuation of amplitude \( \delta V \). The total displacement of a particular Sn atom is the sum of its normal displacement, \( \bar{u} \), plus an excess contribution from volume fluctuations of its nn Ce atoms

\[
\delta u_j = \frac{\bar{u}_j}{V_j} \delta V_j .
\]  

The mean squared vector displacement of the Sn atoms is therefore

\[
<u^2> = <\bar{u}^2> + N<\delta u_j^2>
\]
where \( N \) is the number of \( nn \) Ce atoms for each Sn atom. (The convention \( \langle \delta u^2 \rangle = \langle \delta^2 \rangle / 3 \) is followed throughout this paper.) Here it has been assumed that the normal displacement \( \langle u \rangle \) and the excess displacements, due to the volume fluctuations of different Ce atoms are all uncorrelated. In point of fact locally (intersite) correlated volume fluctuations may be the dominant type of fluctuation in these materials however this is beyond the scope of this paper.

In terms of the experimental results it is possible to use \( \langle \delta u^2 \rangle_{LaSn_3} \) to approximate the normal background \( \langle \delta u^2 \rangle \). The observed anomalous amplitude of vibration \( \delta u^2 \) should then be proportional to \( \langle \delta u^2 \rangle \) which in turn should reflect the mean squared Ce volume fluctuation amplitude \( \langle \delta V^2 \rangle \). We now turn to a calculation whereby the temperature dependence of \( \langle \delta V^2 \rangle \) can be understood.

**Landau Theory**

Adopting the view that the free energy of the system is most nonlinear at a critical volume \( V_c \) one can expand the nonlinear part of the free energy in a Taylor series in the "order parameter" \( V-V_c \), \( V \), \( V \). (See Ref. 24) Dropping terms of higher order than \( V \) yields

\[
F = -a_1 V + a_2 \frac{V^2}{2} + a_4 \frac{V^4}{4}
\]

(6)

The coefficient \( a_4 \) is assumed to be a positive constant for stability and the coefficients \( a_1 \) and \( a_2 \) are assumed to be linearly dependent on \( T \) and \( P \).\(^{24}\)

That is

\[
a_1 = a_1 T + a_1 P \\text{ and } a_2 = a_2 \text{ is } 1, 2
\]

(7)

where \( a_1 T \), \( a_1 P \), and \( a_2 \) are constants.

As usual in such a Landau expansion the conditions \( a_2 < 0 \), \( a_2 = 0 \), and \( a_2 > 0 \) correspond respectively to first order, second order and continuous phase transitions.\(^{24}\) For CeSn_3, \( a_2 = 0 \) is clearly large and positive (the nonlinearity is slight) however for Ce_1-xTh_x and Sm_1-xY_xS all three types of phase transition nonlinearities are observed. In these latter two systems such a phenomenology should be quantitatively accurate near their critical points, whereas in CeSn_3 it is necessary to restrict the discussion to a qualitative one. The free energy change, due to a spatially homogeneous volume fluctuation \( \delta V \), is (to order \( \delta V^2 \)) given by

\[
\delta F = f_1 \delta V + f_2 \frac{\delta V^2}{2}
\]

(8)

where

\[
f_1 = -a_1 + a_2 V + a_4 V^3
\]

(9)

and

\[
f_2 = \frac{a_1 P}{T} = \frac{a_1 T}{\alpha}
\]

(10)

Here, \( K_T = \frac{3 V}{a_1 T} \) and \( \alpha = \frac{3 V}{a_1 T} / P \) are respectively the anomalous contributions to the compressibility and thermal expansion coefficient. The condition \( f_1(\delta V) = 0 \) yields the cubic equation of state\(^{24}\) for the equilibrium value of \( \delta V \) and \( f_1(\delta V) = 0 \) respectively yield \( \alpha \) and \( K_T \). (Terms of order \( \delta V \) in the numerator of \( \alpha \) and \( K_T \) have been neglected)

Of interest here is the temperature dependence of the volume fluctuations of a single Ce atom \( \langle \delta V^2 \rangle \). To extend the macroscopic formalism discussed above to spatially inhomogeneous volume changes the free energy functional (eq.8) must have an additional gradient term of the form \( b/2 \langle (\delta V)^2 \rangle \). The coefficient \( b \) is a positive constant thereby reflecting the surface strain energy associated with a local region of volume differing from the surrounding medium. For simplicity we will consider a local volume fluctuation of average amplitude \( \delta V \) which relaxes to zero in an average linear distance \( \ell \) over a surface of area \( A \). The free energy \( \langle \delta F \rangle \) of such an inhomogeneous volume fluctuation is then (since \( f_1 = 0 \))

\[
\delta F = \frac{b A}{2} \langle \delta V^2 \rangle
\]

(11)

Using this result in the relationship

\[
<\delta V^2> = -\frac{\alpha}{\delta B} \int_0^\infty e^{-\delta B} \delta F \text{ d}(\delta V)
\]

(12)

leads to

\[
<\delta V^2> = \frac{k T}{2} \left[ \frac{b A}{2} + \frac{a_1 P}{K_T} \right]^{-1} = \frac{k T}{2} \left[ \frac{b A}{2} + \frac{a_1 T}{\alpha} \right]^{-1}
\]

(13)

If the values for \( A \) and \( \ell \) appropriate for a single Ce atom are used, then \( \langle \delta V^2 \rangle \) is given by equation 13.

Since \( \delta u^2 \) is this calculation leads to the experimentally observed situation, that \( \delta u^2 \), \( \alpha \), and \( K_T \) all show a strikingly similar temperature dependence. At the same time equation 13 clearly predicts that \( \langle \delta V^2 \rangle \) (and hence the nearest neighbor MSD) will remain finite even if \( \alpha \) and \( K_T \) diverge, as they should at the critical points in the Ce_1-xTh_x and Sm_1-xY_xS systems. In its qualitative predictions for \( \langle u^2 \rangle \) the present phenomenological model agrees closely with the theoretical model of Ghatak and Bennemann.\(^{6}\) In the present model however 1) no assumptions are made regarding the mechanism driving the local volume fluctuations 2) it is possible to derive a direct relationship between \( \langle u^2 \rangle , K_T \), and \( \alpha \), and 3) one can calculate the critical temperature dependence of these quantities.
Critical Behavior

The nonlinearity of CeSn$_3$ is so continuous that the precise critical behavior of $K_T$ and $\alpha$ (appearing in eq.13) is a moot point. However this is not true for the Sm$_{1-x}$Y$_x$S and Ce$_{1-x}$Th$_x$ systems to which the Landau theory also applies. In these alloy systems $a_1$ and $a_2$ are function of $x$ also and the CP occurs at $a_1(T,P,x) = a_2(T,P,x) = 0$. If one approaches such a CP along a line in $T$-$P$-$x$ space specified by $V = V_C$ then the critical divergence in $\alpha$ (or $K_T$) is of the form $(T-T_C)^{-\delta}$, $\delta = 1$. in this mean field model. Along all other pathways the divergence should be of the form $(T-T_C)^{1-1/\delta}$, $\delta = 3$ in this model. In the Ce$_{1-x}$Th$_x$ system this latter behavior is observed. Since the constant temperature approach to the CP in the Sm$_{1-x}$Y$_x$S system ($T_C \approx 200K$ and $x \approx 0.25$) is certainly not along the $V = V_C$ path, the authors would like to point out that (contrary to previous assumptions) the $\delta$ type divergence is to be expected.

Summary

Thus it appears that the anomalous behavior of the Sn MSD in CeSn$_3$ appears understandable in terms of 1) a coupling between the Sn atom displacement and local Ce volume fluctuations, and 2) a continuous, isomorphic phase change occurring at finite temperature. In these respects the behavior of CeSn$_3$ appears analogous to the Ce$_{1-x}$Th$_x$ and Sm$_{1-x}$Y$_x$S systems near their much more violent electronically driven phase transitions.

It should be emphasized that the anomalous lattice properties reported here occur in a limited temperature range centered about 135K (hence the "Finite Temperature" portion of the title). Hence these results are at least consistent with recent neutron scattering results which showed little or no anomalous behavior near room$^{26,27}$ and liquid He temperature. Moreover the local Ce volume fluctuations reported here have been interpreted in terms of thermodynamic fluctuations about the average Ce volume and not in terms of quantum tunneling between Ce valence states. These thermodynamic fluctuations are in general smaller in amplitude and slower in time scale (exhibiting a critical slowing down) than the quantum tunneling process.$^{28}$

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References


25. This is similar to the Landau Girsburg Theory in Superconductivity of Metals and Alloys, W.A. Benjamin, Inc., N.Y., 1966) p. 172.


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