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Authors
Edelstein, A.S.
Fisher, R.A.
Phillips, N.E.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

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A.S. Edelstein, R.A. Fisher, and N.E. Phillips

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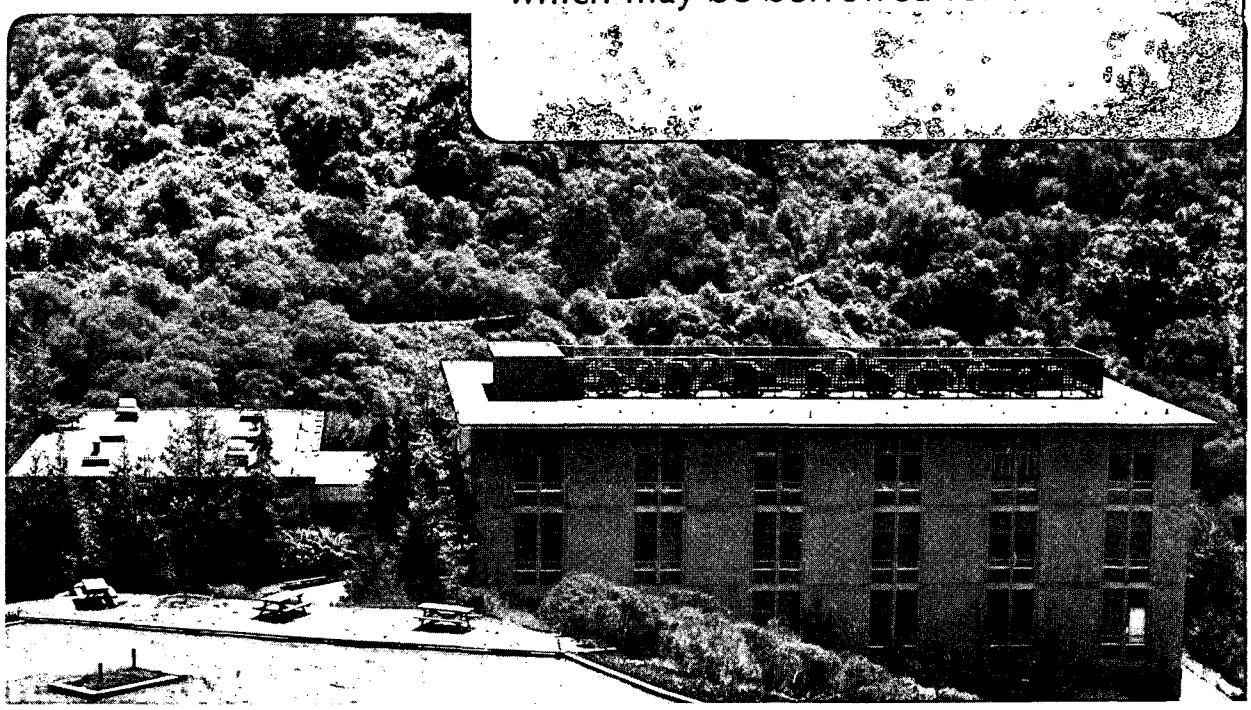

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DISCLAIMER

THE TEMPERATURE DEPENDENCE OF THE SPECIFIC HEAT AND ENTROPY OF $CeAl_3$

A. S. Edelstein, Naval Research Laboratory, Washington D.C. 20375 and

R. A. Fisher and Norman E. Phillips, MMRD, Lawrence Berkeley Laboratory, University of California, Berkeley CA 94720

It is thought that with decreasing temperature $CeAl_3$ first condenses into a crystal-field $J_Z = \pm 3/2$ doublet ground state and then further condenses into a Kondo singlet state. To test this description, we use it to calculate the specific heat and entropy of $CeAl_3$. We calculate the specific heat contribution of the $J_Z = \pm 5/2$ doublet using the resonant level model. The contributions from the $J_Z = \pm 5/2$ and $\pm 1/2$ doublets are computed using the known crystal-field energies but allowing for a broadening of the levels. If it is assumed that the excited crystal-field states have Lorentzian distributions with a width of the order of 50K, the calculation is in generally good agreement with experimental data for the f-electron contribution. (The specific heat of $LaAl_3$, which was measured for the purpose and is reported here, was subtracted from the total to obtain the f-electron contribution.)

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I. Introduction

There has been considerable interest in the fact that the specific heat, C(T), of $CeAl_3$, a heavy-fermion system, can not be fit by Kondo single impurity theory. More specifically, the ratio C/T exhibits a maximum near 0.5K, while Kondo single impurity theory predicts that this quantity increases monotonically with decreasing temperature. One explanation[1] for the maximum is that it is due to a minimum in the density of states, but it can also be explained[2] by a temperature dependent density of states without a minimum. In another approach to a calculation of C(T) at low temperatures, Sticht et al.[3] have combined Fermi-liquid theory and a band-structure calculation. Here we ignore the decrease in C/T below 0.5K, and focus our attention on the f-electron C(T), and particularly the entropy, S(T), over a broader temperature range, T<20K. We compare experimental results for C(T) of $CeAl_3$ with new data for $LaAl_3$ to obtain the f-electron entropy of $CeAl_3$, and we present a model calculation of the f-electron C(T) and S(T) for $CeAl_3$. The calculation is based on a generalization of a model used previously[4] [to calculate the magnetization and magnetic field dependence of C(T)] to include a possible broadening of the excited crystal-field levels by interaction with the conduction electrons. Our motivation for this study was the following: 1) Rice and Ueda[5] predicted that heavy-fermion systems will magnetically order if their multiplicity is only two. Since the crystal-field ground state of $CeAl_3$ is believed

to be a doublet, one might think that their theory predicts that $CeAl_3$ should magnetically order, but no magnetic ordering has been observed[6] for T>20mK. 2) We wished to investigate whether a single impurity Kondo model which includes crystal-field effects could approximately predict the observed C(T) and S(T).

II. Experimental Specific Heat and Entropy

Specific heat measurements on $CeAl_3$, performed on polycrystalline samples, were reported earlier.[2,7] To estimate the phonon contribution we also measured C(T) for a polycrystalline sample of $LaAl_3$. The results, in mJ/mole K, can be represented by

$$C(T) = 4.95T + 0.1213T^3 + 4.13 \times 10^{-4}T^5 - 3.88 \times 10^{-7}T^7, \qquad (1)$$

to within ± 0.5%. We assume that the f-electron contribution is given by subtracting C(T) for $LaAl_3$ from C(T) for $CeAl_3$. The measured C(T) of $CeAl_3$ and $LaAl_3$, and their difference, ΔC, are plotted in Fig. 1. The curve in Fig. 1 representing the specific heat of $CeAl_3$ has been corrected[2] for a small amount of Ce_3Al_{11} (2.6 wt.%) which was present in the sample. One sees, as expected, that the f-electron contribution dominates the specific heat below 10K. The experimental f-electron S(T) was computed by integrating $\Delta C/T$. It is similar to estimates that have been published[8,9] earlier.

III. Model Specific Heat and Entropy

The crystal-field splits the six f-electron J=5/2 state into

three doublets. Neutron scattering experiments[10,11] have established that the crystal-field ground state has $J_Z = \pm 3/2$ and that there are excited state doublets with $J_Z = \pm 5/2$ and $J_Z = \pm 1/2$ at 60.3 and 88.2 K, respectively. In the earlier calculation[4] we assumed that the contribution of the ground state $J_Z = \pm 3/2$ doublet to the magnetization could be calculated by the resonant level model, RLM.[12] We assumed[4] that the contribution of the other two doublets to the magnetization could be calculated using crystal-field theory. We restate the reasoning behind these assumptions. If it were not for the interactions with the conduction electrons, the contribution of the crystal-field ground state doublet to the susceptibility would be proportional to 1/T. These interactions with the conduction electrons give rise to a finite, zero-temperature, spin self-correlation time $\tau = 1/T_K$ (T_K is the Kondo temperature and is believed[1] to be equal to 4.5 K). Because of this correlation time, the factor 1/T in the $J_Z = \pm 3/2$ doublet's contribution to the susceptibility is replaced at low temperatures by $1/T_K$. We used the RLM to incorporate this change. The contributions of the $J_Z = \pm 5/2$ and $J_Z = \pm 1/2$ doublets to the susceptibility are already approximately temperature independent below 10K; therefore they may be less affected by the interactions with the conduction electrons. Since we were only considering the properties of $CeAl_3$ at low temperatures (T<5K), we neglected the interactions of the excited states with the conduction electrons. Thus, we assumed that the energy levels of the excited state doublets were perfectly sharp.

Here, since we are including temperatures as high as 20K, we

shall modify the earlier model[4] to make it more realistic at these higher temperatures by including a broadening of the excited crystal-field states by their interaction with the conduction electrons. The scattering of the conduction electrons by f-electrons in excited states gives rise to the resistivity maximum[13] that occurs near 40K. It is likely that these interactions with the conduction electrons broaden the excited state energy levels. There is experimental evidence[10,11] that these levels are broadened and that their width is of the order 20K. We assume that the energy levels of both excited state doublets are Lorentzian distributions which are centered at the energies determined by the neutron experiments, with full width at half maximum, Γ, which is the same for each doublet.

With these assumptions the f-electron C(T) is given by

$$C(T) = C_{3/2,RLM} + C_{ES,CF}, \tag{2}$$

where $C_{3/2,RLM}$ and $C_{ES,CF}$ are respectively the contributions of the $J_Z = \pm 3/2$ doublet, which is calculated using the RLM, and of the $J_Z = \pm 1/2$ and $\pm 5/2$ excited state doublets, which are calculated using crystal-field theory. The quantity $C_{3/2,RLM}$ is calculated from

$$C_{3/2,RLM} = N_0 \frac{\partial}{\partial T} \int_{-\infty}^{+\infty} E\, N(E)\, f(E/kT)\, dE, \tag{3}$$

where N_0 is Avogadro's number, f is the Fermi function and the RLM density of states is taken to be $N(E) = \Delta/2\pi(E^2 + \Delta^2)$. The normalization of this function is the one obtained by a more detailed theory[14] treating dilute Kondo impurities. The quantity $C_{ES,CF}$ is calculated from

$$C_{ES,CF} = (N_0/k)(\langle E^2\rangle - \langle E^1\rangle^2/\langle E^0\rangle)/T^2\langle E^0\rangle, \tag{4}$$

where k is Boltzmann's constant,

$$\langle E^0 \rangle = 1 + \sum_{j=1}^{2} I(E_j,0,T)/I(E_j,0,\infty), \tag{5}$$

$$\langle E^n \rangle = \sum_{j=1}^{2} I(E_j,n,T)/I(E_j,0,\infty) \qquad n=1,2 \tag{6}$$

and

$$I(E_j,n,T) = \int_0^{+\infty} \frac{E^n}{(E-E_j)^2+\Gamma^2} \exp(-E/kT)dE. \tag{7}$$

In these expressions E_j represents the crystal-field splitting. [The integral in Eq. (7) is carried out only over positive energies. If negative energies were included they would give rise to a large, unphysical contribution at low temperatures because the argument of the Boltzmann factor becomes positive.]

Values of C(T) and S(T) were calculated numerically from these equations using values for the parameters that have been either estimated or measured previously, i.e., Δ=4.5K, E_1=60.3K and E_2=88.2K. The calculation was made for various values of the Lorentzian width including zero (i.e., for sharp crystal-field states). Figures 2 and 3 compare the model predictions with the experimental values of C(T) and S(T). One sees that the fit to both the specific heat and the entropy is improved if one includes the broadening of the excited states. The quality of the fit is best if one uses Lorentzian broadened excited state levels with a width $\Gamma \cong 50$K. Increasing Δ to 6K improves the quality of the fit to C(T), but worsens the fit to S(T). The use of a Gaussian function to represent the broadening of the levels does not provide as good a fit as that obtained with Lorentzians.

The model successfully predicts many of the features of C(T) and S(T) for $CeAl_3$. For the best fits to the experimental data, the excited states have Lorentzian distributions with $\Gamma \cong 50K$ centered at the positions determined by the neutron experiments[10,11]. If the model is correct, the large value for the width of the Lorentzian distributions suggests that it arises because of Kondo-like interactions with the conduction electrons.

The occupancies, $O_{5/2}$ and $O_{1/2}$, of the $J_Z = \pm 5/2$ and $\pm 1/2$ states can be calculated using

$$O_j = I(E_j,0,T)/I(E_j,0,\infty)\langle E^0\rangle. \qquad (8)$$

Even with Γ as large as 50K, because of the Boltzmann factor in Eq. (7), these occupancies go rapidly to zero in the limit $T \to 0$. For this width and T=3K, the largest occupancy is only 1%. Thus, despite the broadening, our results suggest that the low temperature degeneracy of the f-level is still 2. Therefore it seems that the work[5] of Rice and Ueda predicts that $CeAl_3$ should magnetically order at low temperatures.

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FIGURE CAPTIONS

1. Specific Heat of $CeAl_3$ and $LaAl_3$, and their difference, $\Delta C = C(CeAl_3) - C(LaAl_3)$, which is taken to be the f-electron contribution.

2. Comparison of the experimental f-electron specific heat, ΔC, with the model predictions. The solid curve denotes smoothed, corrected values of the experimental data. The dashed curves, representing the model predictions, are labeled by the values of the Lorentzian width, Γ, in K.

3. Comparison of the experimental f-electron entropy with the model predictions. The solid curve denotes the integral of $\Delta C/T$ (see Fig. 1). The dashed curves, representing the model predictions, are labeled by the values of the Lorentzian width, Γ, in K.

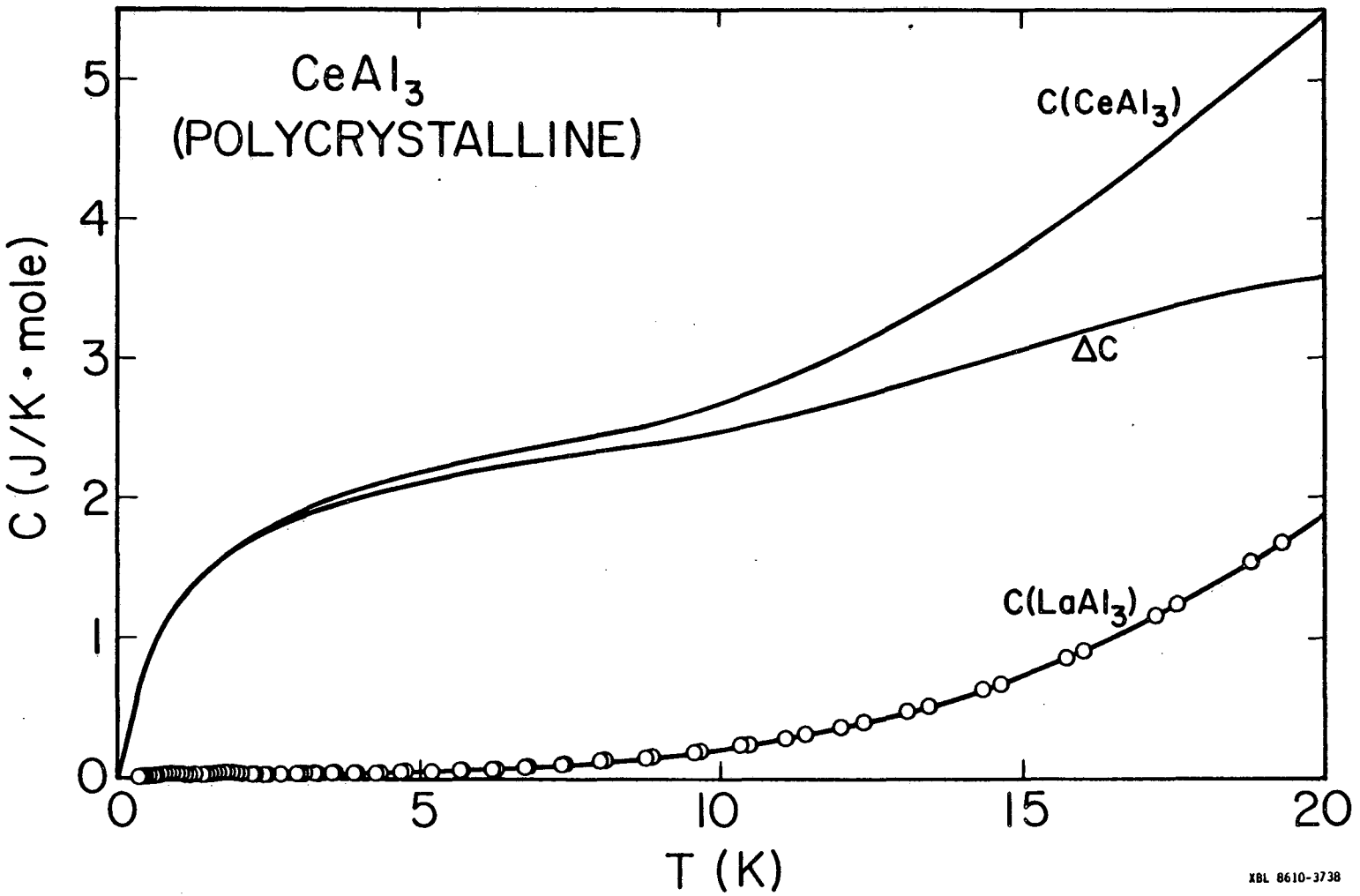
CeAl3
(POLYCRYSTALLINE)
C(CeAl3)
ΔC
C(LaAl3)
C (J/K • mole)
T (K)
0
1
2
3
4
5
0
5
10
15
20
XBL 8610-3738

Fig. 1

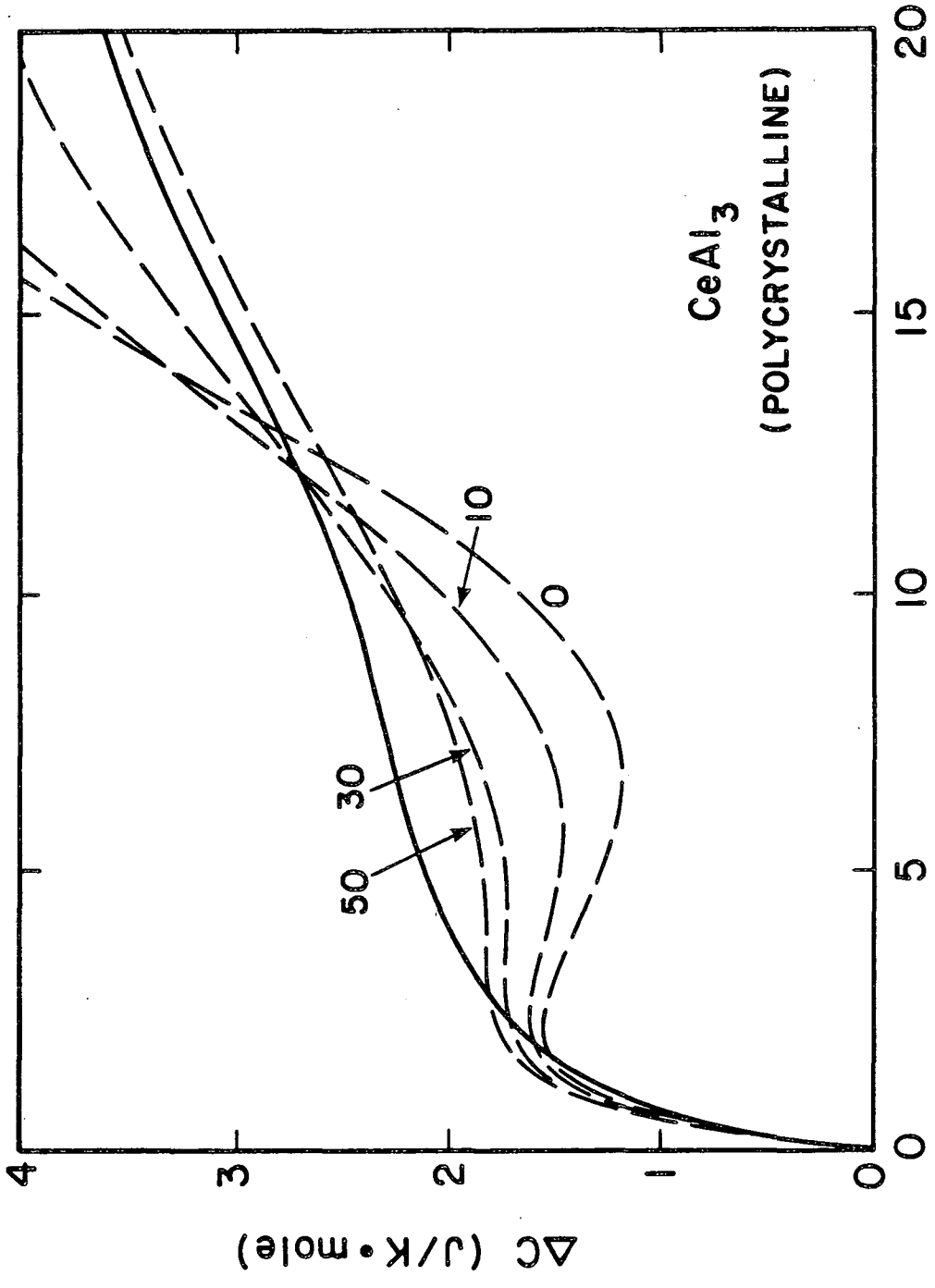

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Fig. 2

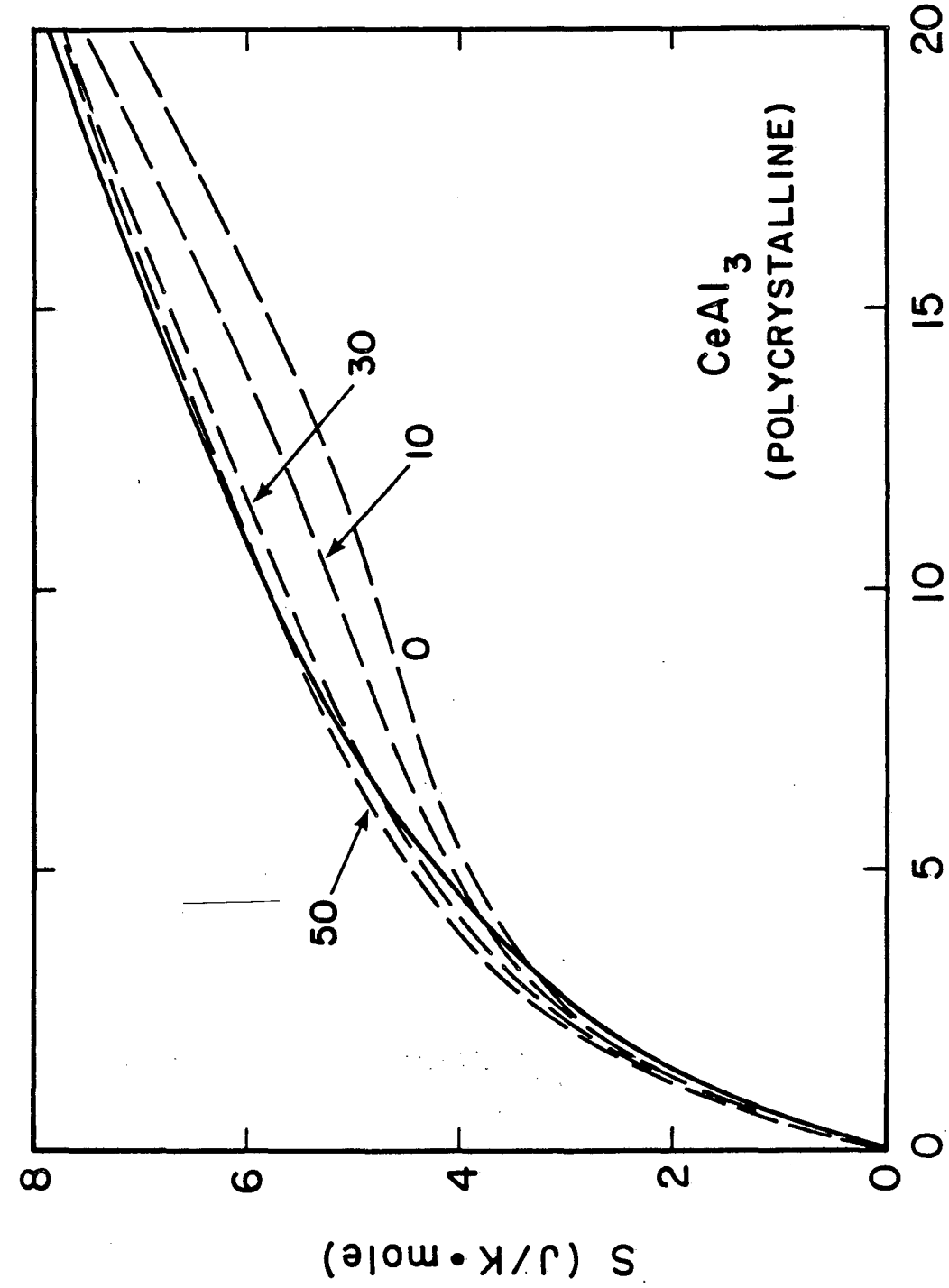

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Fig. 3

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720