Equation of State from a Phenomenological Model for the Kondo System La:Ce†

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Data on the temperature and field dependence of the susceptibility of La:Ce alloys are presented for temperatures $T \geq 0.6$°K and fields up to 50 kG. The data show that the susceptibility $\chi = cF(T, H)$, where F is nearly independent of the concentration c. A phenomenological model predicts a susceptiblitiy which agrees with the experimental $F(T, H)$.

The expression $\chi(T) \propto (T+\theta)^{-1}$ has often been used in describing the susceptibility $\chi(T)$ of Kondo systems for $T \gtrsim T_K$ where $T_K \approx \theta$ is the Kondo temperature. A large departure from this law, which has been attributed to interaction effects, is usually observed at low temperatures. For Cu:Fe alloys, Tholence and Tournier[1] separate the total susceptibility into a single impurity contribution which is of the form $(T+\theta)^{-1}$ and a contribution representing interaction effects which is increasing more rapidly with decreasing T.

Figure 1 shows a plot of χ^{-1} vs T on as-cast arc-melted La:Ce samples which were predominantly in the fcc phase. One sees that above 20°K the susceptibility for this system also fits $\chi = \mu^2/3k(T+\theta)$ with $\theta = 27 \pm 5$°K and $\mu = 2.5\mu_B$. However, for $1.4\text{°K} \leq T \leq 30\text{°K}$ it was demonstrated[3] that $\chi = 5.8\times10^{-4}T^{-1/2}$ emu/g Ce where the concentrations c were $0.02 \leq c \leq 0.20$. Evidence for a $T^{-1/2}$ temperature dependence has also been found in Cu:Cr alloys[4,5] and in $Cr_x Pd_{0.80-x} Si_{0.20}$ alloys[6] $(0.01 \leq x \leq 0.07)$. Susceptibility measurements[7] on $Ce_{0.01}Th_x La_{0.99-x}$ $(x \leq 0.04)$ also give the same susceptibility as one would have in the absence of Th. These data extend the previous result[3] to lower concentrations. One would think that the addition of Th, which increases the scattering probability, would alter the susceptibility if it were due to interaction effects. The resistivity[2] does not show interaction effects at this concentration even at temperatures as low as 0.5°K.

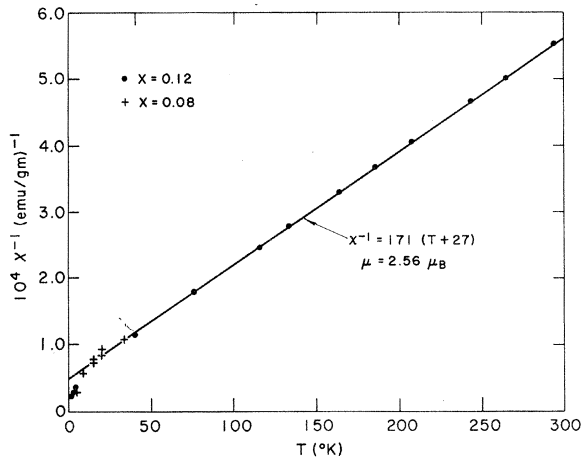

FIG. 1. Reciprocal susceptibility versus temperature for $Ce_x La_{1-x}$ alloys. *Note that from Fig. 1, one expects* $T_K \approx 27$°K and not a much lower value as suggested by Sugawara and Eguchi (Ref. 2).

Resistivity measurements on this system[8] and related systems[9,10] indicate that the Kondo effect is observed at very high concentrations in Ce alloys and compounds. A large concentration range exists for which interaction effects are observed in the resistivity[2,8] but not in the susceptibility.[3] When interaction effects are observed, they resemble those observed in other Kondo systems. The concentrations employed in the resistivity and susceptibility measurements are much higher than those usually employed in work on the Kondo problem. One way of understanding why interaction effects may not be as important in this system is to consider that for a 40-at.% Ce sample the Néel temperature $T_N \approx 4$°K. Hence the interaction energy of a 1-at.% sample is at least as low as 0.1°K and probably lower. It is worth considering why the La:Ce Kondo system might be unusual. The high degree of localiza-

tion of the $4f$ electron of Ce causes the impurity-level width to be very narrow[11] (≈0.01 eV). This property together with the close proximity (≈0.1 eV) of the impurity level to the Fermi level E_F and the large value of U (≈1 eV) makes this system nearly unique. It better satisfies the criteria used by Anderson[12] in studying the Kondo problem, $U \gg E_f \gg \Delta'$ (where U is the Coulomb repulsion term in the Anderson Hamiltonian, E_f is the distance of the impurity f level below E_F, and Δ' is the impurity level width), than nearly any other alloy. For example in Cu:Fe the width Δ' is of order U. It is worth noting that the condition[13] $\Delta' \ll U$ is required to transform the Anderson Hamiltonian to the exchange Hamiltonian. In this sense La:Ce might be an ideal Kondo system; and yet, because of the narrowness of the impurity level, it could have quite different properties than most other Kondo systems.

Here we report measurements on La:Ce alloys of the magnetization $M(T, H)$ and differential susceptibility $\chi(T, H) = \partial M(T, H)/\partial H$. We find that $\chi(T, 0) \propto cT^{-1/2}$ for $0.6°K \leq T \leq 30°K$. In the next section of this Letter we present data which demonstrate that $\chi = cF(T, H)$, where c is the concentration and F is not a function of c. Following this we deduce an equation of state which agrees with our data.

Magnetization measurements have been made on as-cast arc-melted alloys. Figure 2(a) shows a plot of $M(H)/M(10\text{ kG})$ vs H for several alloys for $T \approx 1.4°K$. The data are plotted in this way to emphasize the field dependence; the degree to which the susceptibility is proportional to c is shown in Ref. 3. Clearly, the field dependence of the normalized magnetization is essentially inde-

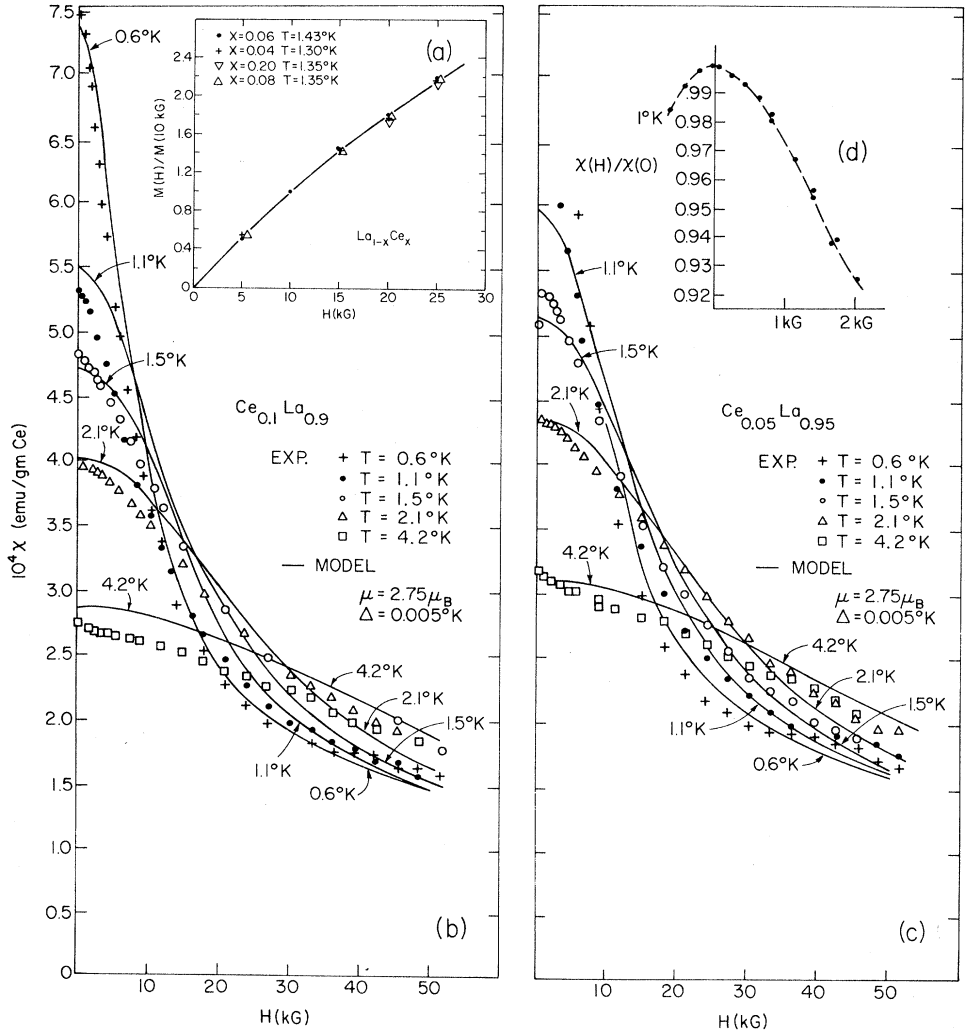

FIG. 2. (a) $M(H)/M(10\text{ kG})$ vs H for several La:Ce alloys; (b), (c) $\chi(H, T)$ vs H for 10- and 5-at.% Ce samples at $T = 0.6$, 1.1, 1.5, 2.1, and 4.2°K; (d) low-field region of χ.

pendent of c.

A more sensitive probe of the field dependence is provided by the susceptibility. The susceptibility data were taken using a standard type of mutual-inductance bridge operating at 30.9 Hz. To avoid eddy-current effects the samples were spark cut into slices 1 mm thick which were insulated from one another. Most of the data were taken on samples which were annealed for two days at 450°C and then rapidly quenched to retain the fcc phase. Shown in Figs. 2(b) and 2(c) is the susceptibility for 5- and 10-at.% Ce samples versus applied field up to 51.4 kG for $T = 0.6$, 1.1, 1.5, 2.1, and 4.2°K. One sees that the susceptibility, in agreement with Ref. 3, is approximately proportional to concentration. More important, in agreement with Fig. 2(a), the magnetic-field dependence of the susceptibility at a given temperature is independent of the concentration. Essentially the same results were obtained after the 5% sample was strain annealed into the double-hexagonal close-packed phase. The added structure sometimes present at very low fields is probably associated in some cases with the presence of ferromagnetic impurities and in other cases with part of the sample becoming superconducting. Because of the latter difficulty the low-field data have been omitted at the lowest temperatures for the 5-at.% sample. Figure 2(d) shows data on another 5% sample which did not have any added structure. We can summarize the present work and that of Ref. 3 by writing $\chi = cF(T, H)$ for the ranges $0.01 \leq c \leq 0.20$, $0 \leq H \leq 18$ kG, $1.4°\mathrm{K} \leq T \leq 300°\mathrm{K}$, and for $c = 0.05$ and 0.10, $0 \leq H \leq 50$ kG, $0.6°\mathrm{K} \leq T \leq 4.2°\mathrm{K}$, where F is nearly independent of c and possibly independent of phase.

In the rest of this paper we present a model[14] which yields an $F(T, H)$ in agreement with experiment and hence provides an equation of state. The first theoretical support for a $T^{-1/2}$ dependence was based upon Anderson's suggestion[12] that the density of states near the Fermi level has the form $N(E) \propto E^{-1/2}$ where E is measured from E_F. More recent theoretical work[15] has shown that this suggestion is unjustified (but not necessarily incorrect). Our justification for using a generalized form of this density of states is that it permits us to calculate an $F(T, H)$ which agrees with our experimental results. We generalize $N(E)$ to include the effects of lifetime broadening and scaling with T_K by taking

$$N(E) \propto [T_K^2(E^2 + \Delta^2)]^{-1/4} \quad (1)$$

for $T < T_K$, where Δ is a level width due to lifetime broadening. We will assume that for $\mu H \ll kT_K$ the magnetization M and susceptibility χ can be computed from

$$M = \mu \int_{-E_F}^{\infty} f(E)[N(E + \mu H) - N(E - \mu H)]\,dE, \quad (2)$$

$$\chi = -\mu^2 \int_{-E_F}^{\infty} (df/dE)[N(E + \mu H) + N(E - \mu H)]\,dE. \quad (3)$$

Equation (3) predicts, in agreement with experiment, that $\chi(T, 0) \propto (T_K T)^{-1/2}$ for $\Delta \ll kT$ or for $\Delta \propto T$. The susceptibility has been computed numerically from Eq. (3) taking $\mu = 2.75\mu_B$ and $\Delta = 0.005°\mathrm{K}$. This value of μ is approximately equal to the high-temperature value (see Fig. 1); however, the agreement using this value is fortuitous since there is no *a priori* reason why μ should have this value. A shift of μ by more than 10% begins to affect the quality of the fit (especially at high fields). The value of Δ used is sufficiently small not to affect the results at the temperatures used in this experiment. The solid curves in Figs. 2(b) and 2(c) show the results of the calculation.[16] The proportionality constants were separately determined for Figs. 2(b) and 2(c). (There is an 8% difference, which is within the accuracy with which we can make an absolute determination of the susceptibility.) The agreement between experiment and the calculation is really quite remarkable. It had been argued in the Ganguly-Shastry[17] derivation of a $T^{-0.6}$ temperature dependence of the zero-field susceptibility that χ would be independent of H until $\mu H \approx kT_K$. At sufficiently low temperatures ($kT < \Delta$) the susceptibility probably becomes temperature independent. In this region[18] we have

$$T_K^{1/4}\chi \propto (\Delta^2 + \mu^2 H^2)^{-1/4} - \frac{d}{dH}\left[\frac{\pi^2 k^2 T^2 H}{12(\Delta^2 + \mu^2 H^2)^{5/4}}\right], \quad (4)$$

where we note that interaction as well as intrinsic effects may give rise to a temperature- and/or concentration-dependent Δ. The susceptibility at high fields ($kT_K \gg \mu H \gg \Delta$ or kT) is proportional to $(HT_K)^{-1/2}$. The observed high-field $H^{-1/2}$ dependence of χ leads either to a rather high value for T_K or to the conclusion that the condition $kT_K \gg \mu H$ is too restrictive.

There are certainly many important questions remaining, not the least of which is this: Why is there this simple dependence upon concentration at such high concentrations? A test of the correctness of the ideas presented here must await

a more complete theoretical treatment of the Kondo problem. What we have demonstrated is that Eqs. (1) and (3) predict a susceptibility which agrees with experiment. If the theoretical assertions turn out to be incorrect, then Eqs. (1) and (2) are at least useful for representing data, i.e., as an empirical equation of state for this system. Work is in progress to see if the magnetic and thermal properties of any other Kondo system can be accounted for by this model.

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Mechanism of the Ferroelectric Phase Transformation in Rare-Earth Molybdates*

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Neutron scattering experiments on $Tb_2(MoO_4)_3$ show the ferroelectric orthorhombic phase to result from a phonon instability at the $(\frac{1}{2}, \frac{1}{2}, 0)$ Brillouin zone corner of the parent tetragonal phase. Anharmonic coupling to these antiferroelectric displacements produces a spontaneous strain which in turn causes a spontaneous polarization through normal piezoelectric coupling. The rare-earth molybdates thus represent a new class of displacive ferroelectric materials *without* a soft *polar* mode.

Borchardt and Bierstedt[1] have shown that $Gd_2(MoO_4)_3$ and the isostructural molybdates of Sm, Eu, Tb, and Dy all undergo ferroelectric phase transformations with transformation temperatures $150°C < T_0 < 190°C$. Subsequent investigations of the dielectric, optical, and mechanical behavior of these materials have revealed several unique and potentially useful properties.[2] The appearance of a spontaneous strain u_s coincident with the spontaneous polarization P_s, coupled with the fact that P_s, u_s states of opposite polarity can be induced by either applied electric fields or mechanical stress, has caused the term ferroelastic to be applied to these materials. There is a small anomalous contribution to the dielectric response of an *unclamped* crystal which appears abruptly upon passing from the higher temperature paraelectric (PE) phase to the ferroelectric (FE) phase and disappears with decreasing temperature. But, remarkably for a ferroelectric substance, this anomalous dielectric contribution disappears when the crystal is *clamped*.[2-4] These observations led Cross, Fouskova, and Cummins[3] to suggest that the transformation is driven by an *elastic instability* and that the P_s is an incidental but necessary consequence of the resulting u_s since the parent PE structure is piezoelectric.

Although this proposal is successful in explaining the apparent "clamping" of the dielectric behavior, it is not entirely satisfying because one should expect that the proposed elastic instability