(the estimates of ΔS for the various heat-capacity ratios are not evidently consistent with the simple Debye model of the lattice), and nothing very definite can be said about quantitative agreement. However, there is definite qualitative agreement for reasonable estimates of the relevant parameters, such as the Raman relaxation time coefficient and the Debye temperature.

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SPIN COMPENSATION IN AN ELEMENT, CERIUM

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The low-temperature susceptibility above the magnetic ordering temperature of La-Ce alloys (Ce concentration ≤ 40 at%) and of α-Ce and β-Ce is proportional to $T^{-1/2}$. This is the temperature dependence recently suggested by Anderson in the case of spin compensation. The susceptibility per Ce atom for the alloys above the magnetic ordering temperature is independent of Ce concentration. It is suggested that these systems exhibit spin compensation.

There has been considerable work[1-8] on alloys which exhibit a Kondo effect (resistivity minimum). The effect occurs when a localized f or d level of an impurity is in close proximity to the Fermi surface of the host. The magnetic moment of the impurity is partially or wholly compensated for by the conduction electrons so that the resulting magnetic moment is greatly reduced.[4,8] Previously these effects have only been investigated in relatively dilute alloy systems. This Letter reports measurements which suggest that spin compensation occurs in the element cerium.

Part of the evidence for the deductions concerning Ce is based on measurements on La-Ce alloys. These alloys exhibit a Kondo effect[9] and large departures from the Abrikosov-Gor'kov (AG) theory[10] of gapless superconductivity. The decrease in the superconducting critical temperature with concentration[11] is larger than predicted by AG. Electron tunneling measurements[12] show that there are more states at low energy than predicted by AG.

Magnetization measurements were initiated to assist in the interpretation of the electron tunneling measurements. The samples were bulk arc-melted alloy samples. X-ray analysis indicated that these samples were predominantly in the fcc phase. Some samples were annealed for 48 h at 600°C and then quenched. These samples were also predominantly fcc. Other samples were annealed for a week at 250°C and then slowly cooled. This procedure produced samples which were approximately 50-50 mixtures of the fcc and double hcp phases. The magnetization measurements gave results which are essentially independent of the heat treatment.

In common with results on other systems exhibiting a Kondo effect it was found that the magnetization did not saturate.[4,13,14] In computing the susceptibility per gram of Ce, $\chi_{\rm Ce}$, from the initial slope of the magnetization versus field curve, it is assumed that the Ce and La contribute additively to the susceptibility. The measured (temperature-dependent) susceptibility of the La, $\chi_{\rm La}(T)$, was employed in the computation. The La sample came from the same batch used in preparing the alloys. The method of analyzing the data is important since it probably explains the difference between the interpretation presented here and that of Sugawara and Eguchi.[9] Sugawara and Eguchi assumed $\chi_{\rm La}$ constant. For the La used in the present work this is not correct. Roberts and Lock's results[15] are similar to those reported here, but there are important quantitive differences.

The values of χ_{Ce} for several alloy samples are shown in Fig. 1. It is seen that the values of the normalized susceptibility χ_{Ce} are independent of the Ce concentration c for $c \leq 20$ at.%. This supports the contention made in Ref. 12 that the large deviations from AG theory seen in tunneling experiments on these alloys having $c \leq 1$ at.% are not due to correlations between the impurity spins. The deviation observed below 4°K for the 40% sample is probably due to antiferromagnetic ordering and is consistent with Roberts and Lock's measurements.[15] Above 4°K the data for this sample agree with the data for all the other samples for $c \leq 20$ at.%. Between the Néel temperature, when present, and 50°K, χ_{Ce} is proportional to $T^{-1/2}$.

Correlations between impurities are not responsible for this temperature dependence, since χ_{Ce} is independent of concentration over such a large concentration range. It has been suggested that the susceptibility of the fcc alloys could be explained as the result of a cubic crystalline-field splitting of the levels into a quartet and a lower doublet.[9,16] Figure 1 shows the prediction of crystalline-field theory[17] with the single adjustable parameter, the splitting between the quartet and the doublet, chosen for best fit to be 150°K. This best fit is clearly inadequate at low temperatures. One could try as was done in Ref. 16 to generalize the crystalline-field theory by including interactions via a molecular-field theory. This would give rise to a concentration-dependent Θ in a Curie-Weiss-type law. This is inconsistent with the concentration independence of the normalized susceptibility.

For comparison purposes Fig. 2 shows data taken by Hurd[2] and Daybell and Steyert[1] on Cu-Fe alloys. Their data also obey a $T^{-1/2}$ dependence at low temperatures. If the susceptibility is multiplied by a constant, their data almost coincide with those for the La-Ce alloys. The susceptibility of Fe in Ir also is proportional to $T^{-1/2}$ at low temperatures.[18] Anderson[19] has suggested this temperature dependence in the case of spin compensation. The dilute La-Ce alloys are in spin-compensated states.[9,11,12] Because χ_{Ce} is independent of concentration over such a large concentration range, one might suppose that all these alloys are in spin-compensated states below 50°K.

This leads one to consider if the same mechanism is important in the pure element Ce. Cerium has a complicated phase diagram.[20,21] At room temperature and under 6-kbar pressure it undergoes a transition which is unique among the elements. It changes from one fcc phase, γ-Ce, to another fcc phase, α-Ce, with a 6% decrease in lattice parameter. It also has a hexagonal phase denoted as β. The phase of Ce at low temperature depends upon its thermal history.[22,23]

Some of Lock's susceptibility data[24] for pure Ce are shown in Fig. 2. The lower curve was obtained upon warming after one cooling. Gschneidner[22] estimated that Lock's sample consisted of 75% α-Ce and 25% β-Ce at 20°K. The upper curve was taken after the sample had been thermally cycled 102 times.[25] Gschneidner estimat-

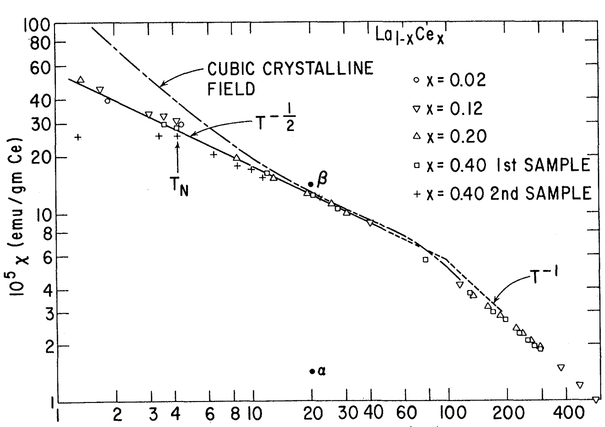

FIG. 1. Susceptibility versus temperature for the La-Ce alloys. The points labeled α and β represent estimates of the susceptibility for the α and β phases of pure Ce.

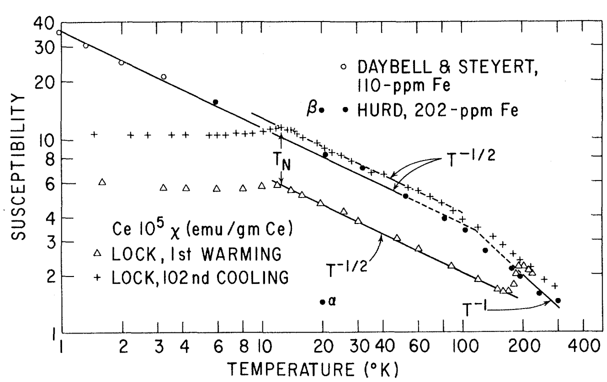

FIG. 2. Susceptibility versus temperature for Cu-Fe alloys and for Ce. The points labeled α and β represent estimates of the susceptibility for the α and β phases of pure Ce. For the Cu-Fe system, $10^{10}\chi$ in emu per gram of alloy per ppm Fe is plotted.

ed that this sample consisted of 38.3% α-Ce and 61.7% β-Ce at 20°K. The changes observed for both samples below 12.5°K are due to antiferromagnetic ordering. Immediately above their Néel points there is a considerable temperature range where the susceptibility for both samples is proportional to $T^{-1/2}$. The susceptibilities of the α and β phases at 20°K are represented by the points labeled α and β in Figs. 1 and 2 and are based upon Gschneidner's estimates of the sample composition. Note that the point β is close to the data for the La-Ce alloys. Below 125°K, where the composition should be constant,[26] the susceptibilities of the α and β phases are linear combinations of the upper and lower curves. Since these curves represent $T^{-1/2}$ temperature dependences one can conclude that the susceptibility of the α and β phases is proportional to $T^{-1/2}$. My preliminary measurements on Ce are consistent with this, but do not give as good a fit to this power law.

If the decreased moment of α-Ce is due to a promotion or partial promotion of the $4f$ electron into the conduction band, one would expect an increase in the number of conduction electrons. Position annihilation measurements[27] show no evidence of this sort of increase in the number of conduction electrons. Recently Coqblin and Blandin[21] have suggested that the α-γ transition is due to a condensation into a spin-compensated state. Following their suggestion, we made a set of hypotheses which provide a consistent explanation of all the above facts.

(1) Both phases of Ce and the alloys are in spin-compensated states when their susceptibilities are proportional to $T^{-1/2}$.

(2) When they are in these states the interactions between spins are very small.

(3) The susceptibility is given by

$$\chi = CT^{-1}f(T/T_K); \tag{1}$$

$$f = 0.4(T/T_K)^{1/2}, \quad T \lesssim T_K,$$
$$= 1, \quad T \gg T_K, \tag{2}$$

where C is the Curie constant per gram of Ce. Equation (1) is the form one would expect for a system of noninteracting impurities. Equation (2) gives the observed dependence at low temperature and allows the theory to scale with the Kondo temperature. The high-temperature form of the susceptibility represents a Curie law or the high-temperature limit of a Curie-Weiss law. The function f is proportional to the square of the spin-compensated moment. The model predicts that $f \to 0$ as $T \to 0$, and hence, the ground state is a singlet.

Because the La-Ce and Cu-Fe alloys have nearly the same temperature dependence, Eq. (1) predicts that their Kondo temperatures are similar; i.e., $\approx$16°K. One can also estimate T_K for the alloys from[6]

$$T_K \simeq E_0 \exp[-\tfrac{1}{3}|J|N(0)]. \tag{3}$$

Using Sugawara's determination[11] of $J = -0.053$ eV and the free-electron estimates of $E_0 = 7.9 \times 10^4$ °K and $N(0) = 0.66$ eV^{-1}, one finds $T_K \approx 5.7$°K. The agreement between the two estimates is satisfactory considering the crudeness of the latter estimate. The high-temperature data indicate that the Curie constant per gram of Ce is approximately the same for the alloys and Ce. It will be assumed that all the phases of Ce have the same Curie constant. As discussed above, the low-temperature susceptibility of β-Ce is similar to that of the La-Ce alloys and so β-Ce by applying Eqs. (1) and (2) also has $T_K \approx 16$°K. Using the ratio of the susceptibilities for the two phases as determined from the points α and β of Fig. 1 and Eqs. (1) and (2) one finds for α-Ce that $T_K \approx 1600$°K. This value is very approximate since it is very sensitive to the estimates of composition. Considering the large uncertainties involved, this value of T_K for α-Ce is reasonably close to the critical point,[20,21] $T_c = 575 \pm 25$°K, for the γ-α transition. This is the temperature at which the two phases become indistinguishable. Thus Coqblin and Blandin[21] may be correct in their supposition that a transition into a spin-compensated state provides the driving force for the γ-α transition. This is possible since the f level in Ce is only 0.076 eV below the Fermi surface.[28]

Specific-heat measurements[15] on these alloys also show one and possibly two anomalies above T_N which may be associated with spin compensation. They are not connected with any simple antiferromagnetic transition since there is no corresponding change in the susceptibility. One of these anomalies is, however, a strong function of concentration.

The addition of La inhibits the γ-to-α transition since it decreases the driving force per unit volume. If α-Ce is a spin-compensated state with a high Kondo temperature one can understand how it will have a small moment without a large change in the conduction-electron density.

Obviously the interpretation given here is rather speculative but it provides insight into an important problem, the nature of the α-γ transition. Previous explanations are not consistent with all facts. The explanation given here is not completely new.[21] The $T^{-1/2}$ temperature dependence and the concentration independence of the normalized susceptibility are new and provide evidence for the interpretation. Further the concentration independence shows that the large deviations from the AG theory of gapless superconductivity[11,12] are not due to spin correlations and instead are probably associated with spin compensation. The estimates of T_K even for the dilute alloys should be considered as tentative. Work is in progress on testing the ideas presented here. If they are correct they open several new possibilities. For example, one could study the transformation from a spin-compensated state into an antiferromagnetic state. Are the spins forming the antiferromagnetic state still spin compensated? They probably are. Is cerium unique or do other elements behave in a similar manner?

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