Magnetic susceptibility of the dense Kondo system $CeAl_3$†

E. Borchi, S. De Gennaro, and C. Taddei
Istituto di Fisica Teorica dell'Università, Firenze 50125, Italy
(Received 27 December 1976)

A previous calculation of the magnetic susceptibility of intermetallics of cerium in a cubic lattice is extended to the case of a hexagonal structure. In particular, numerical calculations for the $CeAl_3$ intermetallic are presented. These provide quantitative support to the suggestion that the $CeAl_3$ compound is a dense Kondo system.

The cerium intermetallic compounds have received considerable experimental and theoretical attention in recent years. Particular attention has been devoted to some systems which seem to present the Kondo effect. In fact, although the Kondo effect was originally observed in dilute cerium alloys where isolated impurities can be considered as noninteracting entities, several authors[1,2] suggested that concentrated cerium systems might behave like dilute systems.

In particular the magnetic susceptibility of some intermetallic cerium compounds has been shown to present low-temperature anomalous properties which have been tentatively interpreted in terms of the Kondo effect.[2-4]

In a recent work[5] two of the present authors have given a complete calculation of the magnetic susceptibility for cerium compounds which takes into account the Kondo effect, the crystalline field which acts on the cerium ion, and the magnetic interaction among the cerium ions. This calculation was carried out for a cerium ion in a cubic lattice and, as an application, the case of the intermetallic compound $CeIn_3$ was considered.

Recently another cerium compound, the intermetallic $CeAl_3$,[4,6-8] has received considerable attention for its anomalous low-temperature properties which resemble the Kondo effect.

A quantitative estimate of the magnetic susceptibility for this system should therefore be of great aid in establishing if the Kondo effect is present (or not). However, as this compound crystallizes in a hexagonal Ni_3Sn-type structure, a new calculation is necessary in order to correctly take into account the effects of the crystalline environment around the cerium ion.

In this paper then we present the calculation of the magnetic susceptibility for a cerium intermetallic compound in a hexagonal lattice. Since, from a conceptual point of view, this calculation follows the same scheme adopted in our previous work,[5] here we will limit ourselves to simply giving the final results. Using these theoretical results we will show, thus giving quantitative support to the suggestion by several authors,[4,6-8] that the presence of the Kondo terms is essential in order to produce good agreement with the experimental data even in the concentrated system $CeAl_3$.

However, in order to clarify our approach to the problem, we also want to remark that our calculation derives from a perturbative approach to the Kondo problem so that it is scarcely reliable for temperatures lower than the characteristic Kondo temperature T_K ($T_K \gtrsim 1$ K for the $CeAl_3$ system[4]). For this reason the region of temperatures $T \lesssim 1$ K is beyond the scope of our work and thus we had no reason to confirm or to contend several recent semiquantitative interpretations of the $CeAl_3$ very-low-temperature properties which appear to be very anomalous for $T \lesssim 1$ K.[4,7-9] We only point out that recent neutron-scattering measurements[10] at $2 < T < 300$ K have shown the $CeAl_3$ system to present a localized (nonhybridized) $4f^1$ configuration so that the simple s-f exchange Hamiltonian appears to be appropriate to our calculation.

Following our previous works[5,11] the magnetic susceptibility for a concentrated Kondo system can be written

$$\chi = \frac{\chi^{(0)}}{1-(\Theta/T)F(T)} + \chi^{(2)}, \tag{1}$$

where $\chi^{(0)}$ is the magnetic susceptibility evaluated taking only the crystal field into account, $\chi^{(2)}$ is the Kondo term evaluated in the presence of the crystal field and the term $\Theta F(T)$, which is defined in Ref. 5, takes into account the magnetic interaction among cerium ions.

For a cerium ion in a hexagonal environment the $\chi^{(0)}$ and $\chi^{(2)}$ terms have been previously evaluated in the case of an applied magnetic field parallel to the c axis of the crystal.[11] In the case of a field perpendicular to the c axis of the crystal, following the same lines of Ref. 11, we obtain after a laborious but straightforward algebraic calculation:

$$\chi_{\perp}^{(0)} = \frac{C}{T}\frac{3}{35}(1+e^{-\beta\Delta_1}+e^{-\beta\Delta_2})^{-1}\left(9+\frac{16}{\beta\Delta_1}(1-e^{-\beta\Delta_1})+\frac{10}{\beta(\Delta_1-\Delta_2)}(e^{-\beta\Delta_2}-e^{-\beta\Delta_1})\right), \tag{2}$$

$$\begin{aligned}\chi_{\perp}^{(2)} = {} & \frac{C}{T}[2n(E_F)\Gamma]^2\frac{3}{140}(1+e^{-\beta\Delta_1}+e^{-\beta\Delta_2})^{-1} \\ & \times\Bigg[180J_1(0)+144J_1(\Delta_1)+72(1-e^{-\beta\Delta_1})[J_3(\Delta_1)+J_1(\Delta_1)]-16(1-e^{-\beta\Delta_1})J_1(\Delta_1)\left(\frac{2}{\beta\Delta_1}-\frac{5}{\beta(\Delta_1-\Delta_2)}\right) \\ & +20e^{-\beta\Delta_2}(1-e^{-\beta(\Delta_1-\Delta_2)})J_1(\Delta_1-\Delta_2)\left(\frac{4}{\beta\Delta_1}+\frac{5}{\beta(\Delta_1-\Delta_2)}\right)+72J_2(\Delta_1)+80\left(\frac{1}{\beta\Delta_1}+\frac{1}{\beta(\Delta_1-\Delta_2)}\right)^2 \\ & \times[e^{-\beta\Delta_1}J_2(\Delta_1)+e^{-\beta\Delta_1}J_2(\Delta_1-\Delta_2)-J_2(\Delta_1)+J_2(\Delta_2)-e^{-\beta\Delta_2}J_2(\Delta_2)-e^{-\beta\Delta_2}J_2(\Delta_1-\Delta_2)] \\ & +50e^{-\beta\Delta_1}\frac{J_2(\Delta_1-\Delta_2)}{\beta(\Delta_1-\Delta_2)}(1+e^{-\beta(\Delta_2-\Delta_1)})+80e^{-\beta\Delta_1}\left(\frac{J_2(\Delta_1)}{\beta(\Delta_1-\Delta_2)}+\frac{J_2(\Delta_1-\Delta_2)}{\beta\Delta_1}\right) \\ & +\frac{J_2(\Delta_1)}{\Delta_1}(128e^{-\beta\Delta_1}-160)+(1+e^{-\beta\Delta_1}+e^{-\beta\Delta_2})^{-1}\left(9+\frac{16}{\beta\Delta_1}(1-e^{-\beta\Delta_1})+\frac{10}{\beta(\Delta_1-\Delta_2)}(e^{-\beta\Delta_2}-e^{-\beta\Delta_1})\right) \\ & \times[5J_2(\Delta_1-\Delta_2)(e^{-\beta\Delta_1}-e^{-\beta\Delta_2})+8J_2(\Delta_1)(e^{-\beta\Delta_1}-1)]\Bigg],\end{aligned} \tag{3}$$

where C is the Curie constant and Δ_1 and Δ_2 are the crystal-field splittings defined according to the energy-level diagram reported in Fig. 1. The other symbols have the same significance as in Ref. 11.

Using these expressions and the results of Refs. 5 and 11, the magnetic susceptibility $\chi = \frac{1}{3}(\chi_{\parallel}+2\chi_{\perp})$ is evaluated in terms of the parameters Δ_1, Δ_2, $n(E_F)\Gamma$, and Θ (the value of the half bandwidth D, which does not appreciably affect the physical results, has been taken $D = 800$ K as in previous works). As far as the crystal field parameters Δ_1 and Δ_2 are concerned, they have been obtained from previous calculations and measurements by other authors.[7,12,13] The three disposable sets of Δ_1, Δ_2 values are very different from one another so that, even if the values obtained by Murani *et al.*[13] using neutron inelastic scattering are probably the most reliable, we prefer, for the sake of completeness, to evaluate the magnetic susceptibility for all the existing sets of Δ_1, Δ_2 values. Once the parameters D, Δ_1, Δ_2, have been established, the s-f exchange constant $n(E_F)\Gamma$ and the temperature Θ remain the only disposable parameters in our calculation.

Moreover, since the value of $n(E_F)\Gamma$ significantly influences the magnitude of the susceptibility only in the low-temperature region where the $\chi^{(2)}$ term is appreciable (for $T \lesssim 20$ K), the value of Θ is practically fixed by the high-temperature values of the magnetic susceptibility where $\chi \cong \chi^{(0)}/(1 - \Theta/T)$.

In Fig. 2(a) we report the theoretical results and the available experimental data[4,12] for the reciprocal magnetic susceptibility in the region $1 \leq T \leq 20$ K. Also reported are the different sets of parameters which correspond to the different theoretical curves. Particularly good agreement between theory and experiments is obtained in the range of temperatures 1–4 K where the Kondo effect should be more effective. From $T \simeq 4$ K to $T \simeq 20$ K the different experiments tend to give divergent results so that some new careful experimental data are needed for a meaningful comparison with the theory. However, the fact that the theoretical results lie inside the two different sets of experimental data is greatly encouraging.

Also reported in Fig. 2(b) are the results obtained by putting $\Gamma = 0$, or without s-f exchange interaction taken into account. The disagreement between theory and experiments, especially in the region $T = 1$–4 K, clearly shows the Kondo effect is essential in order to produce a correct interpretation of the $CeAl_3$ low-temperature properties.

For the sake of completeness Fig. (3) reports on the measured and theoretical inverse magnetic

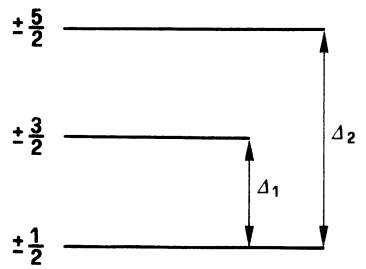

FIG. 1. Energy-level diagram for the $^2F_{5/2}$ state of Ce ions in a hexagonal crystal field.

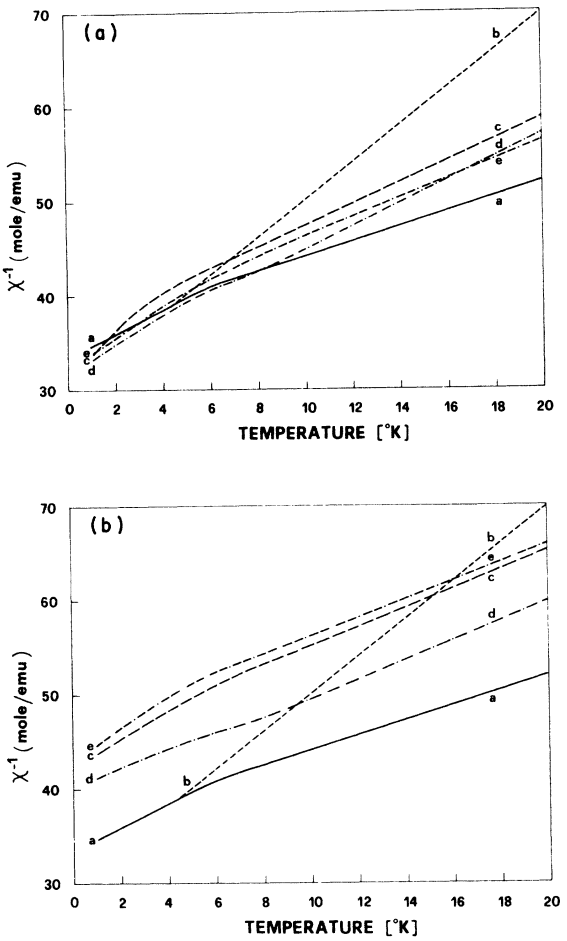

FIG. 2. (a) Temperature variation of the reciprocal susceptibility in $CeAl_3$. Curves (a) and (b) report the experimental data as obtained in Ref. 4 and in Ref. 12, respectively. Curves (c), (d), and (e) report the theoretical results obtained using the following values of the parameters: curve (c) $\Delta_1 = -56$ K, $\Delta_2 = 224$ K, $\Theta = -19$ K, $n(E_F)\Gamma = 0.045$; curve (d) $\Delta_1 = -32$ K, $\Delta_2 = 82$ K, $\Theta = -22$ K, $n(E_F)\Gamma = 0.033$; curve (e) $\Delta_1 = -83$ K, $\Delta_2 = -22$ K, $\Theta = -22$ K, $n(E_F)\Gamma = 0.05$. (b) Temperature variation of the reciprocal susceptibility in $CeAl_3$. Curves (a) and (b) are the same as in Fig. 2(a). Curves (c), (d), and (e) have been evaluated for the same values of the parameters as in Fig. 2(a) but with $\Gamma = 0$.

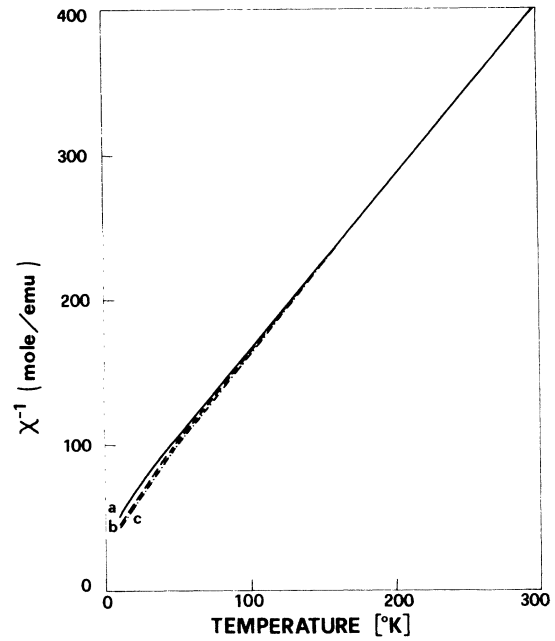

FIG. 3. Temperature variation of the reciprocal susceptibility in $CeAl_3$. Curve (a) reports the experimental data as obtained in Ref. 12. Curves (b) and (c) have been evaluated using the same values of the parameters as in curve (c) and (d), (e) of Fig. 2(a), respectively.

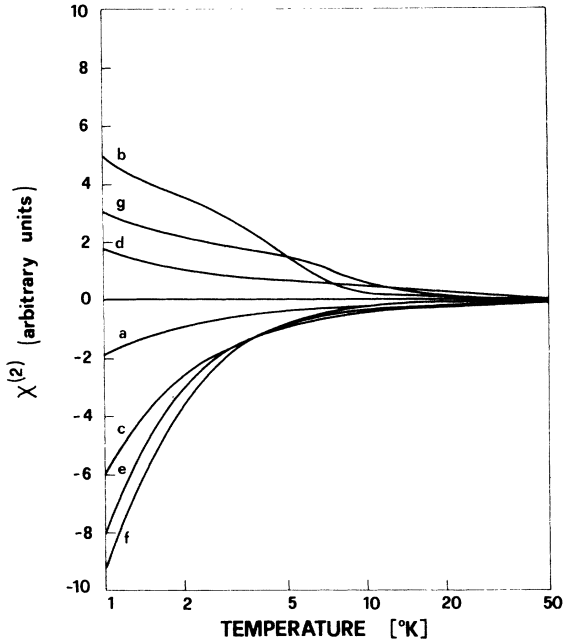

FIG. 4. Temperature variation of the second-order contribution to the magnetic susceptibility in $CeAl_3$ for various choices of the crystal-field parameters Δ_1 and Δ_2: curve (a) $\Delta_1 = -20$ K, $\Delta_2 = -50$ K; curve (b) $\Delta_1 = -20$ K, $\Delta_2 = -10$ K; curve (c) $\Delta_1 = \Delta_2 = 0$ K; curve (d) $\Delta_1 = 50$ K, $\Delta_2 = -50$ K; curve (e) $\Delta_1 = 20$ K, $\Delta_2 = 50$ K; curve (f) $\Delta_1 = 50$ K, $\Delta_2 = 20$ K; curve (g) $\Delta_1 = -20$ K, $\Delta_2 = 50$ K.

susceptibility for all the available experimental range of temperatures. As it is easily seen, no appreciable difference derives from using the different sets of parameters in the high-temperature region $T \gtrsim 70$–80 K.

Finally, to conclude, we would like to mention an interesting result which emerges from our calculation. It has been often disputed which doublet state, among $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, $|\pm\frac{5}{2}\rangle$ states, is the ground state in $CeAl_3$. Our calculation allows us to

exclude that the $|\pm\frac{1}{2}\rangle$ doublet state is the ground state in $CeAl_3$. In fact, as it is easily seen in Fig. 4, where the $\chi^{(2)}$ term is reported for the various choices of the doublet ground state, only if the $|\pm\frac{3}{2}\rangle$ or $|\pm\frac{5}{2}\rangle$ is the doublet ground state, the $\chi^{(2)}$ contribution may be positive thus bending downward the χ^{-1} vs. T curve in the low-temperature region in agreement with the experimental results.

†Work supported in part by the National Research Council.

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