Magnetic susceptibility of La:Ce†

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A previous calculation of the crystal-field effects on the magnetic susceptibility of La:Ce alloys is extended in order to take into account all the contributing terms besides the logarithmically divergent ones. Numerical calculations show that previous neglected terms are of considerable importance in the low-temperature range and cannot be ignored if a reliable result is required.

A theoretical treatment of the crystal-field effects on the magnetic susceptibility of a Kondo system was given in a recent paper by the present authors.[1] The case of a cerium ion in a cubic crystal field was examined and the theoretical results were compared with the experimental data on the La : Ce system.

Owing to the exceeding complication of the algebraic calculation only divergent $\ln(K_B T)$ terms were taken into account; the other terms were neglected under the assumption that they are of some relevance only at relatively high temperatures, where the entire (second-order) exchange contribution was reasonably estimated to be negligible with respect to the zero-order one.

On the other hand, in a recent work[2] we also examined the influence of the crystal field on the magnetic susceptibility of Y-Ce alloys. In the Y : Ce alloys the hexagonal crystal-field Hamiltonian is diagonal with respect to the eigenstates of J_z (the component of the angular momentum parallel to the c axis of the crystal). Due to this favorable feature it was relatively simple to accomplish an exact calculation of the magnetic susceptibility for Y : Ce taking all the contributing terms into account. This calculation showed that, even if the divergent $\ln(K_B T)$ terms can be considered as predominant in the whole range of temperatures, other second-order terms are, however, not completely negligible if a reliable result is required. For this reason we think it to be of some importance to make here an exact (up to the second order in the coupling constant Γ) evaluation of the magnetic susceptibility for La : Ce alloys also.

As this calculation is a simple (although laborious) algebraical extension of the previous calculation on La : Ce alloys[1] and follows exactly the same lines as in the work on Y : Ce alloys[2] here we will limit ourselves to give simply the final results and to perform a new comparison with available experimental data.

We obtain, as in Ref. 1, for the zero-order term

$$\chi^{(0)} = \frac{C}{T}\frac{4}{7}\frac{1}{1+2e^{-\beta\Delta}}\left[\tfrac{1}{12}(26e^{-\beta\Delta}+5) + \frac{8}{3}\frac{1}{\beta\Delta}(1-e^{-\beta\Delta})\right], \quad (1)$$

where $C=(g\mu_B)^2 J(J+1)/3K_B$ is the Curie constant for one cerium ion per volume unit ($g=\frac{6}{7}$ and $J=\frac{5}{2}$), Δ is the crystal-field splitting, and $\beta=1/K_B T$. The next nonvanishing term, which is of the second order in the coupling constant Γ, is much more involved than in Ref. 1. We obtain

$$\chi^{(2)} = (g\mu_B)^2\Gamma^2 \frac{5}{81}\frac{1}{1+2e^{-\beta\Delta}}\sum_{\vec{k}\vec{k}'} f_k(1-f_{k'})$$
$$\cdot\Big\{(-125-986e^{-\beta\Delta})\left(\frac{2}{(\epsilon_k-\epsilon_{k'})^3}+\frac{\beta}{(\epsilon_k-\epsilon_{k'})^2}\right) - 1120\left(\frac{1}{(\epsilon_k-\epsilon_{k'}-\Delta)^3}+\frac{e^{-\beta\Delta}}{(\epsilon_k-\epsilon_{k'}+\Delta)^3}\right)$$
$$-320\frac{\beta}{(\epsilon_k-\epsilon_{k'}-\Delta)^2} - \frac{800\beta e^{-\beta\Delta}}{(\epsilon_k-\epsilon_{k'}+\Delta)^2} - \frac{512e^{-\beta\Delta}}{\Delta(\epsilon_k-\epsilon_{k'}+\Delta)^2} + \frac{512}{\Delta(\epsilon_k-\epsilon_{k'}-\Delta)^2}$$
$$+400\frac{\beta}{\Delta}e^{-\beta\Delta}\left(\frac{1}{\epsilon_k-\epsilon_{k'}-\Delta}-\frac{1}{\epsilon_k-\epsilon_{k'}}\right) + 1552\frac{\beta}{\Delta}e^{-\beta\Delta}\left(\frac{1}{\epsilon_k-\epsilon_{k'}}-\frac{1}{\epsilon_k-\epsilon_{k'}+\Delta}\right)$$
$$+1440\frac{\beta}{\Delta}e^{-\beta\Delta}\frac{1}{1+2e^{-\beta\Delta}}\left(\frac{1}{\epsilon_k-\epsilon_{k'}}+\frac{1}{\epsilon_k-\epsilon_{k'}+\Delta}-\frac{2}{\epsilon_k-\epsilon_{k'}-\Delta}\right)$$
$$-640(1+e^{-\beta\Delta})\frac{1}{\Delta^2(\epsilon_k-\epsilon_{k'})} + 640\frac{1}{\Delta^2(\epsilon_k-\epsilon_{k'}-\Delta)} + 640e^{-\beta\Delta}\frac{1}{\Delta^2(\epsilon_k-\epsilon_{k'}+\Delta)}$$

$$+240\beta^2 e^{-\beta\Delta}\frac{1}{1+2e^{-\beta\Delta}}\left(\frac{2}{\epsilon_k-\epsilon_{k'}-\Delta}-\frac{1}{\epsilon_k-\epsilon_{k'}+\Delta}-\frac{1}{\epsilon_k-\epsilon_{k'}}\right)\Bigg\}, \quad (2)$$

where the sums are performed on the electron states $\vec{k}$ and $\vec{k}'$ and f_k is the Fermi-distribution function.

It is easily seen that, by correctly allowing for the $\Delta\to 0$ limit, the expression of $\chi^{(2)}$, in absence of the crystal field, is obtained,[3]

$$\chi^{(2)}_{\Delta\to 0}=-\frac{C}{T}4\Gamma^2\sum_{\vec{k},\vec{k}'}f_k(1-f_{k'})\left(\frac{1}{(\epsilon_k-\epsilon_{k'})^2}+\frac{2}{\beta(\epsilon_k-\epsilon_{k'})^3}\right). \quad (3)$$

For the numerical evaluation of $\chi^{(2)}$ we make use of the J_1, J_2, J_3 functions which have been defined and computed in Ref. 2. We obtain

$$\chi^{(2)}=(C/T)[2n(E_F)\Gamma]^2\Psi(T) \quad (4)$$

where

$$\Psi(T)=\frac{1}{189}\frac{1}{1+2e^{-\beta\Delta}}\Bigg\{(125+986e^{-\beta\Delta})[J_1(0)-J_3(0)]-560[J_3(-\Delta)+e^{-\beta\Delta}J_3(\Delta)]+160[2J_1(-\Delta)+5e^{-\beta\Delta}J_1(\Delta)]$$
$$+512\frac{1}{\beta\Delta}[e^{-\beta\Delta}J_1(\Delta)-J_1(-\Delta)]+\frac{e^{-\beta\Delta}}{\beta\Delta}J_2(-\Delta)\left(400-\frac{2880}{1+2e^{-\beta\Delta}}\right)+\frac{1}{\beta\Delta}J_2(\Delta)\left(\frac{1440e^{-\beta\Delta}}{1+2e^{-\beta\Delta}}-1552e^{-\beta\Delta}\right)$$
$$+640\frac{1}{\beta^2\Delta^2}[J_2(-\Delta)+e^{-\beta\Delta}J_2(\Delta)]+240e^{-\beta\Delta}\frac{1}{1+2e^{-\beta\Delta}}[2J_2(-\Delta)-J_2(\Delta)]\Bigg\}. \quad (5)$$

Here the symbols have the same significance as in Ref. 2. Keeping only the logarithmically divergent terms, as in Ref. 1, we would obtain

$$\Psi'(T)=\frac{1}{189}\frac{1}{1+2e^{-\beta\Delta}}(125+986e^{-\beta\Delta})[J_1(0)-J_3(0)]$$
$$=\frac{1}{189}\frac{1}{1+2e^{-\beta\Delta}}(125+986e^{-\beta\Delta})\times\ln(2.62K_BT/D). \quad (6)$$

It has to be remarked that Eq. (6) correctly replaces the result previously given in Eq. (13) of Ref. 1, where an algebraical miscalculation produced some spurious terms.[4] Coming back to the complete expression (5) of $\Psi(T)$, we now search for the values of the parameters Δ and $|n(E_F)\Gamma|$ that fit the experimental data. As the half-bandwidth D does not appreciably affect the physical results, we assume D to be in a range typical of the rare-earth alloys $D=500-1000$ K.

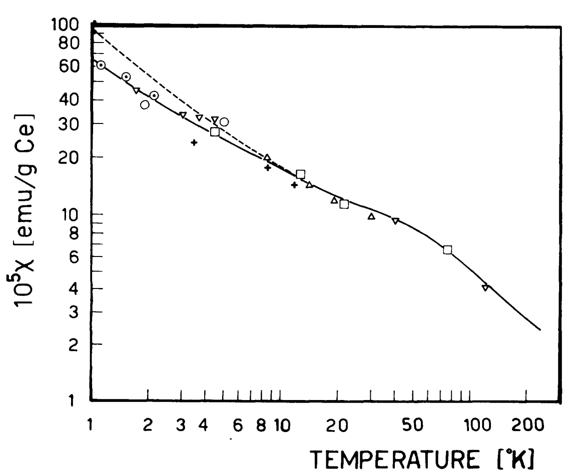

FIG. 1. Susceptibility vs temperature for the La : Ce system. The continuous curve gives the predictions of the theory. The dashed line shows the zero-order contribution plus the logarithmically divergent term. The experimental points are taken from Ref. 5 and [⊙] from Fig. 2 (c) of Ref. 6 (in the limit $H\to 0$).

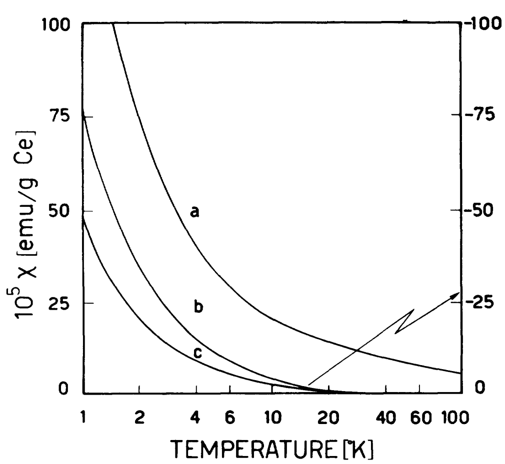

FIG. 2. Contributions to the magnetic susceptibility vs T for the following choice of the parameters: $\Delta=120$ K, $n(E_F)$ $\Gamma=0.076$, and $D=750$ K. (a), zero-order contribution $\chi^{(0)}$; (b), second-order contribution $\chi^{(2)}$; (c), logarithmically divergent contribution. Note that the (b) and (c) values have been reported on a negative scale.

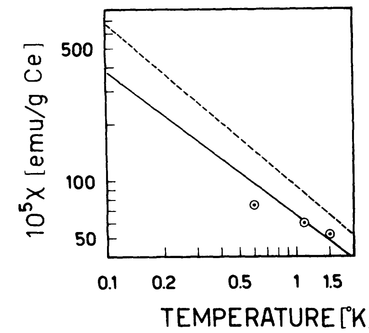

FIG. 3. Susceptibility vs. temperature in the very-low temperature region. The continuous curve gives the predictions of the theory. The dashed line shows the zero-order contribution plus the logarithmically divergent term. The experimental points are taken from Ref. 6.

Allowing for a variation of Δ in a broad range of temperatures, 30–300 K, and assuming $|n(E_F)\Gamma|$ in the region of typical values, 0.05–0.10, we may obtain a good fit to the experimental data for $\Delta = 110-130$ K and $n(E_F)\Gamma = 0.07-0.08$.

In order to make a comparison, the experimental points[5,6] and the theoretical curve for the magnetic susceptibility are shown in Fig. 1 for the following values of the parameters: $\Delta = 120$ K, $n(E_F)\Gamma = 0.076$, and $D = 750$ K. Moreover, in order to provide useful information on the general theoretical behavior of the magnetic susceptibility, we report the various terms contributing to the susceptibility in Fig. 2. As in the Y : Ce alloys case[2] the zero-order contribution $\chi^{(0)}$ appears to be largely dominant everywhere but in the very-low temperature range. From Figs. 1 and 2 it is also apparent that in the very-low temperature range the divergent $\ln(K_B T)$ terms do not give an adequate description of the entire second-order contribution $\chi^{(2)}$. By using the previous reported[1,7] expression of the resistivity for La : Ce and the values of the parameters which give a good fit to the experimental points [$\Delta = 110-130$ K, $n(E_F)\Gamma = 0.07-0.08$, $D = 500-1000$ K], we may also evaluate the Kondo temperature T_K, defined as the temperature where perturbation theory breaks down. We obtain for the Kondo temperature $T_K = 0.4-0.8$ K, which is in good agreement with the values previously found by several authors[8-13] ($T_K < 1$ K).

Though it is unlikely that our calculation is valid for $T \lesssim T_K$, in Fig. 3 we report on, for completeness, the calculated values of the magnetic susceptibility in the very-low temperature region 0.1–1.5 K. Also reported are the available experimental points at 0.6, 1.1, and 1.5 K.[6] As far as the experimental point at 0.6 K is concerned we must note that its value is obtained in Ref. 6 from a sample with 10-at. % Ce concentration. The other examined sample, with 5-at. % Ce, not only does not give a clearly defined value for the magnetic susceptibility in the limit $H \to 0$, but clearly shows, as a function of the magnetic field H, a different behavior from the more concentrated sample. For this reason we think the experimental point at 0.6 K to be not completely reliable.

However, if other experiments would confirm in future the reported experimental value at 0.6 K, it would be evident from Fig. 3 the breakdown of the perturbation theory for $T \simeq 0.6$ K, that is when T approaches the previously determined Kondo temperature T_K.

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