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# 4*f*-Virtual-Bound-State Formation in $CeAl_3$ at Low Temperatures

K. Andres and J. E. Graebner
*Bell Laboratories, Murray Hill, New Jersey 07974*

and

H. R. Ott
*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule,*
*Hönggerberg, Zürich, Switzerland*

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Specific-heat and electrical-resistivity measurements in $CeAl_3$ below 0.2 K reveal enormous magnitudes of the linear specific-heat term $C=\gamma T$ ($\gamma=1620$ mJ mole/K$^2$) and the $T^2$ term in $\rho=AT^2$ ($A=35$ $\mu\Omega$ cm/K$^2$). We conclude that the 4*f* electrons obey Fermi statistics at low temperatures because of the formation of virtual bound 4*f* states.

In the intermetallic compound $CeAl_3$ both the lattice parameters and the susceptibility at high temperatures suggest that the Ce ion is in a 3+ state. The lack of magnetic order at low temperatures is interpreted as being caused by a partial admixture of the nonmagnetic 4+ state. Such behavior has been explained in different ways in the past. A model distinguishing between "atomic" and "bandlike" 4*f* electrons has been suggested by Gschneidner.[1] More recently, $CeAl_3$ has often been cited as an example of a mixed valence—or interconfigurational fluctuation (ICF)—compound[2]; and in another approach, Mott[3] has explained the peculiar properties of $CeAl_3$ based on a Kondo-type theory. The purpose of this note is to present new data on the very-low-temperature properties of $CeAl_3$ and to show that they can be understood using Friedel's[4] classic theory of virutal bound states.

All measurements were performed in dilution refrigerators except the thermal-expansion measurement, which was done in a $^3$He cryostat. The data were taken by standard techniques using a cerium-magnesium-nitrate magnetic-susceptibility thermometer. Only polycrystalline samples were investigated; they were cut from a 20-g button that was arc melted in argon and annealed at 900°C for 3 weeks. X-ray analysis showed the proper structure (hexagonal, $Ni_3Sn$-type). The specific-heat results are shown in Fig. 1. Below 150 mK, the specific heat varies linearly with temperature and yields an extremely large $\gamma$ value of 1620 mJ/mole K$^2$. It remains practically unchanged in a field of 10 kOe except at the lowest temperatures where the nuclear Zeeman specific heat of the Al nuclei is seen (the $Ce^{140}$ and $Ce^{142}$ isotopes have no nuclear spin). This behavior is to be contrasted with what one would have expected from the lowest-lying $Ce^{3+}$ Kramers doublet state, namely a strong field-dependent magnetic specific heat with entropy $R\ \ln 2$/mole. Interpolating our data with previous specific-heat measurements down

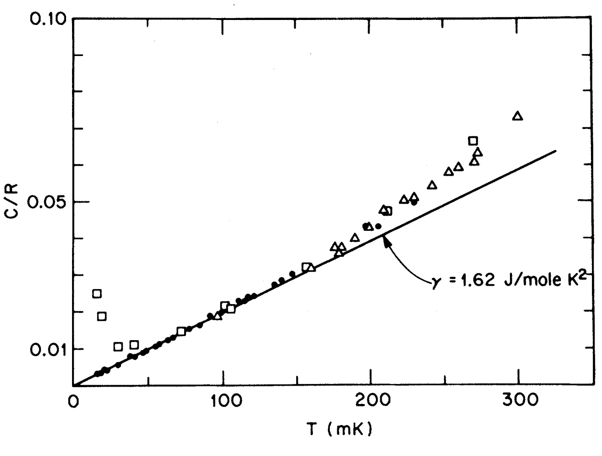

FIG. 1. Specific heat of $CeAl_3$ at very low temperatures in zero field (●, △) and in 10 kOe (□).

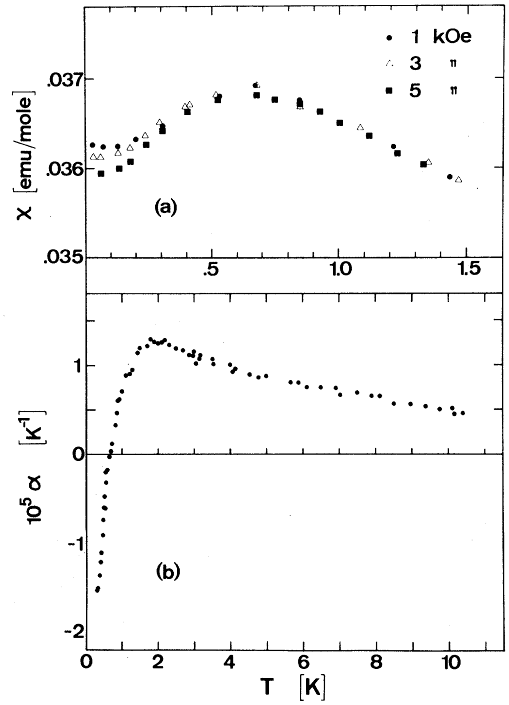

FIG. 2. (a) Susceptibility of polycrystalline $CeAl_3$ in different magnetic fields below 1.5 K. (b) Linear thermal-expansion coefficient of a polycrystalline sample of $CeAl_3$ below 10 K.

to 1.2 K,[5] we find that the entropy from 0 to 1 K is only 27% of $R$ ln2 and is thus reduced below its classical value. The results of Ref. 5 indicated that the first excited doublet lies about 10 K above the ground state and that again about 20% of the entropy for this doublet is missing.

Susceptibility measurements on $CeAl_3$ down to 0.5 K have been presented before by Edelstein *et al.*[6] At high temperatures,[7] Curie-Weiss behavior, characteristic of $Ce^{3+}$, is observed. At low temperatures, the susceptibiltiy gradually flattens out. We observe a very weak susceptibility maximum around 0.6 K [shown in Fig. 2(a)] which is field independent up to 5 kOe and which we believe to be a genuine property of $CeAl_3$, rather than an impurity effect. Below 0.1 K we find $\chi = 0.036$ emu/mole.

The very low-temperature resistivity is shown in Fig. 3. It displays an unusually strong and exact $T^2$ dependence. In $\rho = \rho_0 + AT^2$, $A$ equals 35 $\mu\Omega$ cm/K$^2$. This temperature dependence continues up to 0.3 K. At higher temperatures, a somewhat slower and more linear increase is observed.[6]

In order to search for a valence change from

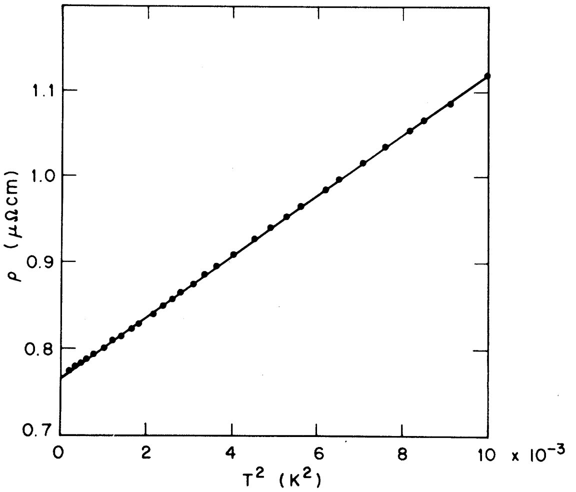

FIG. 3. Electrical resistivity of $CeAl_3$ below 100 mK, plotted against $T^2$.

$Ce^{3+}$ to $Ce^{4+}$ we have measured the thermal contraction from 295 to 4.2 K as well as the thermal-expansion coefficient below 10 K. At 295 K, the lattice parameters of $CeAl_3$ are characteristic of $Ce^{3+}$.[8] The volume change $-\Delta V/V$ upon cooling to 4.2 K is $1.5\times10^{-3}$, much less than the one expected for a 3+ to 4+ valence change which would result in a volume collapse of order $(4-10)\times10^{-2}$. The low-temperature thermal-expansion coefficient [shown in Fig. 2(b)] is anomalous in that it changes sign at 0.65 K and seems to go through a negative maximum below 0.3 K.

The specific-heat, susceptibility, and resistivity data of $CeAl_3$ at very low temperature all demonstrate conclusively that the $4f$ electrons of the $Ce^{3+}$ ions obey Fermi statistics in this region. The high-temperature data,[5,7] on the other hand, can be explained quite well (except at the lower temperatures) by assuming Boltzmann statistics of uncoupled $4f$ states ($^2F_{5/2}$) which are crystal-field split into three Kramers doublets. If the low-temperature behavior were due to rapid fluctuations between the $Ce^{3+}$ and $Ce^{4+}$ states, we would expect the volume of the crystal to shrink anomalously upon cooling from room temperature, which is not observed. A natural explanation of the low-temperature behavior is the formation of virtual bound $4f$ states of widths narrower than the crystal-field splitting. From the ambivalent nature of Ce it is known that the energy of its $4f$ state is close to the Fermi energy; in the case of $CeAl_3$ we postulate that its location is right at the Fermi energy and that the crystal-field splitting actually raises the highest doublet state above the Fermi energy. The very-low-temperature properties can then be explained by the fact that coherence develops among the lowest-lying virtual bound states (which emerge from the lowest-lying $J=|\pm\frac{3}{2}\rangle$ doublet states) of the individual Ce ions. Such coherence arises because the $Ce^{3+}$ scattering centers become identical at low temperatures leading to a definite phase correlation among virtual bound states. A band of collective states with an extremely high density is thus formed, to which the Fermi energy is pinned at low temperatures. The degeneracy temperature of these states is related to the molar electronic-specific-heat coefficient by

$$\gamma_e = \tfrac{1}{2}\pi^2 nR/T_F \tag{1}$$

($n$ is the number of $f$ electrons per Ce ion, $n=1$) and yields $T_F \simeq 25.3$ K from our measurement. If, on the other hand, the susceptibility is interpreted as a Pauli spin susceptibility, we have

$$\chi_p = 3L\mu_B{}^2/2K_\beta T_F \tag{2}$$

which would yield $T_F = 15.6$ K. Both estimates are of course very rough, neglecting the energy dependence of the effective mass and also neglecting exchange effects. The order of magnitude however is correct since the width of the virtual $4f$ states should be equal to or smaller than the distance to the first-excited doublet state (~ 10 K). We would like to mention here that Varma and Yafet[9] have recently arrived at very similar conclusions in a much more formal way by treating the mixed-valence problem in the case of strong $s$-$f$ interactions (i.e., when the $f$ levels are close to the Fermi energy).

We thus assume that three doublet states transform into virtual bound states. At high temperatures all three of these states are partially (and equally) occupied because the intra-atomic Coulomb interactions require that the number of $4f$ electrons per Ce ion cannot increase above one. As long as the virtual bound states do not overlap, Boltzmann statistics are then restored at high temperatures and we can explain the observed reduction in crystal-field entropy of the first excited doublet[5] by a partial overlap of the ground and first excited virtual bound states.

This model also offers an alternative explanation of the striking resistivity anomaly at 37 K which has been observed previously in $CeAl_3$,[10,11] namely, that the resistivity increases from a room-temperature value of 65 $\mu\Omega$ cm to a maximum of ~ 140 $\mu\Omega$ cm at 37 K and then drops to a residual value of 0.7 $\mu\Omega$ cm. As the crystal is cooled from high temperatures to the region where $kT$ equals the overall crystal-field splitting (~ 50 K), more conduction electrons can scatter resonantly with the three virtual bound states, which are initially equally populated. This leads to an increase in resistivity. However, when the $f$ electrons start condensing into their ground states, the scattering at the Ce ions becomes more and more coherent and leads to the dramatic decrease in resistance below 37 K. According to Friedel[4] the maximum contribution to the resistivity (in the incoherent regime) can be

$$\Delta\rho_{\max} \leq [4\pi c\hbar/(e^2 k_F p)](2l+1). \tag{3}$$

With $l=3$ ($4f$ angular momentum quantum number), $c=0.25$ (concentration of Ce ions), $p=3$ electrons/atom, and a free-electron value of the Fermi wave vector $k_F = (3\pi^2 p/V)^{1/3} = 1.6\times10^8$ cm$^{-1}$, we obtain $\Delta\rho_{\max} = 188$ $\mu\Omega$ cm. This is in order-of-magnitude agreement with the peak value observed at 37 K (140 $\mu\Omega$ cm).

Previously, the increase in resistance with decreasing temperature above 37 K has been explained by Maranzana[12] as a "Kondo side-band effect." It is argued that since spin-flip scattering processes are only possible within the excited $j_z = |\pm\frac{1}{2}\rangle$ doublet and between the $j_z = |\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$, $|\pm\frac{5}{2}\rangle$ doublets (the $|\pm\frac{3}{2}\rangle$ being the ground state), the Kondo effect does not exist at low temperatures but Kondo resonances occur away from the Fermi energy by an amount equal to the energy differences between the doublet states. This is in contrast with the prediction by Kondo[13] that when the degeneracy of the magnetic ion is lifted, the Kondo resonance at $T=0$ should disappear rather than be shifted to a finite temperature. Also, it has been shown by susceptibility and Knight-shift measurements[14] that the exchange energy $\Gamma'$ in the Hamiltonian

$$H = -\Gamma' \vec{J}\cdot\vec{s} \tag{4}$$

is positive, favoring parallel alignment of $\vec{J}$ and $\vec{s}$, which would rule out an ordinary Kondo effect.

As suggested before by Mott,[3] we interpret the $T^2$ dependence of the resistivity below 0.3 K as an interband scattering effect between conduction electrons and the band of collective states. Baber[15] finds for the $T^2$ term in the resistance due to electron-electron scattering the approximate formula

$$\rho \simeq \frac{\pi^2 e^2 m^2 \cdot 71.06}{16nh^3}\left(\frac{T}{T_F}\right)^2, \tag{5}$$

where $m$ is the free-electron mass, $n$ the $s$-electron density, and $T_F$ the degeneracy temperature of a heavy-mass band. Here the heavy-mass electrons are assumed to interact with the $s$ electrons via a screened Coulomb interaction and a screening length of 1 Å has been assumed arbitrarily. According to (5), $T_F$ would have to be 2.7 K to agree with our observations, somewhat smaller but still in order-of-magnitude agreement with what we deduced from the specific heat and the susceptibility. It is interesting to note that if we apply Kaiser and Doniach's[16] spin-fluctuation theory to $CeAl_3$, we can get a very good fit to the resistivity data up to ~1 K [where $\rho(T)$ varies more linearly with temperature] when assuming a spin-fluctuation temperature of 2.5 K. However, we do not believe that this theory applies here, because we do not see the predicted *reduction* $\sim T^3 \ln(T/T_F)$ from the linear specific heat $\gamma T$ (which would amount to 15% at 0.3 K). Rather, we observe an *increase* over $\gamma T$ which we ascribe to the proximity of the first excited virtual bound state. Also, measurements of Edelstein *et al.*[6] in 40 kOe show a small *positive* magnetoresistance below 0.5 K rather than a negative one as one might expect if one suppresses spin fluctuations.

We would like to point out again that our virtual-bound-state model is similar to the recently proposed model of the mixed-valence state by Varma and Yafet,[9] one difference being that the latter neglects the crystal-field splitting of the $4f$ electron. Their ground-state wave function is also a mixture of localized $4f$ and extended $s$ states, and the density of states is similar to that of a virtual bound state of width $\Gamma$ located $\Delta\epsilon$ below the Fermi energy. The effective number of $4f$ electrons per Ce ion depends on the ratio of $\Delta\epsilon/\Gamma$. In the case of $CeAl_3$ this number would be close to 1, and in that case Varma and Yafet do indeed predict a susceptibility anomaly like the one we observe. They also predict (in the same temperature range) a decrease in the $4f$ charge density with increasing temperature. Our negative thermal expansion from 0 to 0.65 K could be interpreted as being due to a decrease in $4f$ charge density of about $(1.5-4)\times10^{-4}$, which is roughly an order of magnitude less than what is predicted. This disagreement however could be due to the neglect of the crystal-field splitting (i.e., of higher-lying virtual bound states) in the Varma-Yafet model.

In conclusion we think that the remarkable and unusual very-low-temperature properties of $CeAl_3$ can be well understood in terms of our heuristic model of coheherent $4f$ virtual bound states which is qualitatively equivalent to the mixed-valence state recently proposed by Varma and Yafet.

We would like to acknowledge enlightening discussions with Dr. C. M. Varma, and to thank S. Darack for his help with the specific-heat measurements.

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