Magnetic Susceptibility of Cerium Metal Under Pressure

M. R. MacPherson* and G. E. Everett*
University of California, Riverside, California 92502

and

D. Wohlleben† and M. B. Maple†
University of California, San Diego, La Jolla, California 92037
(Received 22 September 1970)

The demagnetization of the $4f$ state of metallic Ce as function of pressure was studied by magnetic susceptibility measurements. In contrast to the β and γ phases, the collapsed α phase does not show a local moment but exhibits instead a strong local exchange enhancement of the susceptibility. The susceptibility decreases linearly with increasing pressure in our measuring range and is estimated to decrease by 80% between the boundaries of the magnetic and the superconducting phases. The results are consistent with the Anderson model of local moment formation over the entire range of interest of the parameter $E_{4f}-E_F$.

In the β and γ phases cerium exhibits an effective moment very close to the value of the singly occupied $4f$ shell, and the β phase undergoes an antiferromagnetic transition at 12.5°K.[1] On the other hand, in the α' phase above ~50 kbar, Wittig found superconductivity at 1.8°K.[2] Since cerium is the only metal known to have a magnetic and a superconducting phase, it is of paramount interest for studies of local moment formation and the interplay of magnetism and superconductivity, especially in the intermediate α phase.

We have developed a technique to measure small paramagnetic susceptibilities under pressure allowing, for the first time, unambiguous magnetic studies of the α phase. Our results are consistent with a demagnetization of the local $4f$ state on the Ce atom according to the Friedel-Anderson model[3] which has been applied[4] to Ce with the assumption that the energy of the local $4f$ level E_{4f} moves upwards with respect to the Fermi level E_F when the pressure increases. It seems that Ce is suitable for quantitative experimental and theoretical studies of many aspects of the Friedel-Anderson model over a very wide range of the fundamental parameter $E_{4f}-E_F$.

The samples were arc melted from ingots (Johnson-Matthey batch No. 269, nominal purity 99.99%) in an argon atmosphere and machined into cylinders. They were annealed at 300°C for about 5 h, fitted into Teflon jackets, and pressurized in a small clamp (1.2 by 0.6 in. in diameter) made of very pure BeCu. The magnetic moment of this assembly was measured as a function of magnetic field (0 to 11 kG) and temperature (0.38 to 300°K) in a Faraday magnetometer described elsewhere.[5] The large diamagnetic moment of the fairly massive clamp was compensated by a strip of pure Ta sheet of suitable length which was wrapped around its diameter. The residual magnetic moment of the empty clamp assembly was measured separately as a function of field and temperature. The absolute accuracy of the susceptibility, after correction for the clamp, is about 1%, whereas the relative accuracy (between changes of pressure) is 0.3%.

Figure 1 shows the pressure dependence of the

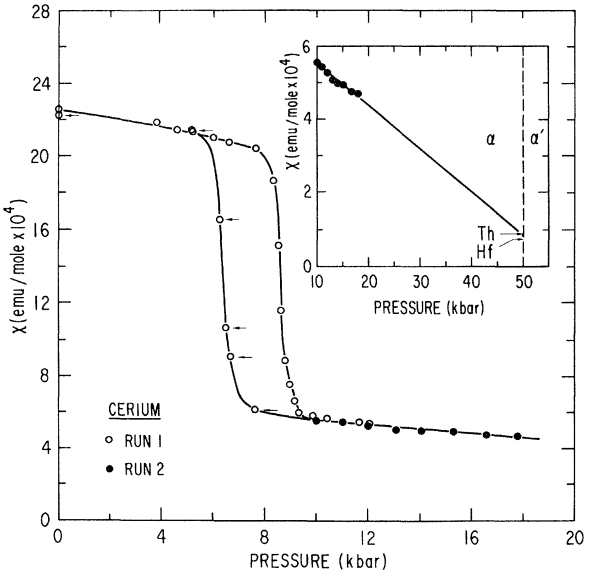

FIG. 1. Pressure dependence of the magnetic susceptibility of cerium at room temperature. The inset shows the linear extrapolation of the measurements in the α phase to the α-α' phase boundary. The extrapolated susceptibility at 50 kbar is comparable with the susceptibilities of the quadrivalent transition metals Hf and Th.

susceptibility of Ce at room temperature. The values represent the slopes of the magnetization curves (differential susceptibility $\chi \equiv dM/dH$) at 8 kG. A drastic drop of the susceptibility coincides with the well known γ-to-α phase transition[6] near 7.6 kbar and shows qualitatively the same hysteresis in pressure as the sample volume monitored during the application of pressure. There is an appreciable decrease of χ with increasing pressure in both the γ and α phases. In the α phase this decrease is 20% between 8 and 18 kbar and is linear in pressure within experimental accuracy. It extrapolates, at 50 kbar, to $\chi = (85 \pm 15) \times 10^{-6}$ emu/mole, suggesting that the susceptibility might drop by about 80% between the magnetic and the superconducting phase boundaries. The scatter of the data is due to uncertainties in the pressure.

Figure 2 shows the temperature dependence of the differential susceptibility of α-Ce at 10 kbar. It is nearly temperature independent above 100°K but shows a low-temperature rise with a small maximum near 3°K. The overall temperature dependence is very weak compared with that of the β phase,[1] suggesting that α-Ce is basically a Pauli paramagnet, i.e., that there is no local magnetic moment in this phase.

In order to determine whether the low-temperature tail is intrinsic or due to magnetic impurities, a mass spectroscopic analysis was performed on the sample of Fig. 2,[7] which yielded a total rare-earth–impurity saturation magnetization of 5.3×10^{-3} emu/mole Ce (assuming the moments of the three-valent ions), in fairly good

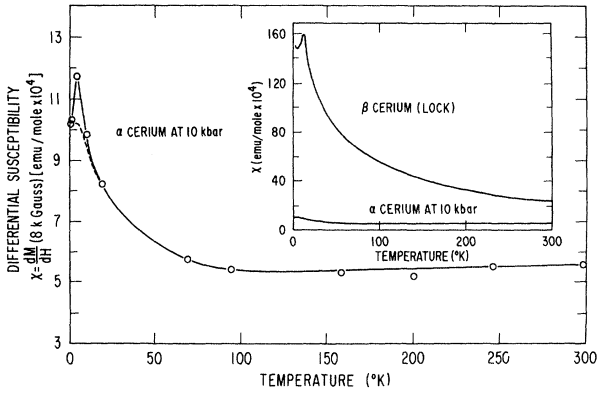

FIG. 2. Temperature dependence of the differential susceptibility of α-Ce at 8 kG and 10 kbar. A correction for a small concentration of paramagnetic impurities is indicated by the dashed line. The inset emphasizes the weak temperature dependence of the nonmagnetic α phase by a comparison with the β phase.

agreement with our value of 7.5×10^{-3} emu/mole Ce obtained from magnetization curves at 0.4°K. The direct magnetic measurement is considered more reliable, since the mass spectroscopic analysis suffers from large uncertainties in the absolute determination of the impurity concentration. The differential susceptibility of the impurities was calculated as a function of temperature, using the relative impurity concentrations from the analysis. It was then scaled with our saturation moment and applied as a correction to the sample susceptibility, as indicated by the dashed line in Fig. 2. This correction removes the maximum at 3°K. (The maximum, incidentally, may definitely not be regarded as an indication of antiferromagnetic ordering. It does not occur in the direct susceptibility $\chi \equiv M/H$. A maximum is expected between 1 and 3.5°K in the differential susceptibility of rare-earth ions in a field of 8 kG.)

Clearly, most of the rise of the susceptibility below 100°K is not due to magnetic impurities. At this point, it is uncertain whether it is an intrinsic property of α-Ce or whether it is due to the presence of some residual β- or γ-phase material (1-2%). We favor the first possibility for various technical reasons.

Although α-Ce carries no local moment, it has very unusual magnetic properties. From the available electronic specific-heat data[8] one finds for the unrenormalized exchange enhancement χ_{meas}/χ_γ either 8 or 4.2, depending on whether one regards the low-temperature rise as intrinsic or not. This exchange enhancement and the molar susceptibility itself are very large and only comparable with Pd in the periodic system. The strong exchange enhancement explains the absence of superconductivity in this phase[8,9] (above 0.3°K at 10 kbar). On the other hand, at the α-α' phase boundary, the room-temperature susceptibility extrapolates to a rather low value which is very close to that of Th ($\chi = 88 \times 10^{-6}$ emu/mole) and Hf ($\chi = 75 \times 10^{-6}$ emu/mole), the two four-valent superconducting transition metals which are most closely related to four-valent Ce. Thus, at high pressure, α-Ce behaves like a normal transition metal, whereas at low pressure the presence of the $4f$ level is still felt strongly.

The large exchange enhancement suggests that there might be considerable changes of the magnetic moment of dilute rare-earth impurities in α-Ce due to conduction-electron polarization, in analogy with the cases of Gd in Pd[10] and Sc.[11] We have therefore studied the temperature depen-

dence of the susceptibility and, in particular, the saturation magnetization at 0.4°K of 0.59 % of Gd in α-Ce at 10 kbar. We find a Curie-Weiss law and a saturation moment of $(7.3 \pm 0.2)\mu_B$ per Gd impurity, very close to the value of ferromagnetic Gd itself. Thus there is no unusual conduction-electron polarization. We interpret this to mean that the large exchange enhancement is on local, not itinerant, electrons.

The behavior of the susceptibility of Ce as a function of pressure and temperature can be understood in terms of the Friedel-Anderson model[3] for localized magnetic states in metals. This model, although originally designed for dilute impurities, was applied to the $4f$ state on the ions of Ce metal by Coqblin and Blandin[4] who argue that because the spatial extent of the $4f$ shell is one order of magnitude smaller than the lattice constant of the rare-earth metals, the width of a hypothetical $4f$ band due to overlap of neighboring $4f$ shells is not only much smaller than the width of the $6s$ and $5d$ bands, but seems to be even smaller than the broadening of the $4f$ state in a single cell due to interactions with the conduction electrons (i.e., smaller than the width of the virtual bound $4f$ state). This view has recently received support from experiments with Ce impurities in La, Th, and related metals[12] which show a Ce $4f$ virtual level width of about 10^{-2} eV coinciding with estimates of the width of the $4f$ states (or $4f$ band) in metallic Ce.[4,13] Thus, the $4f$ bandwidth in metallic Ce is either equal to or, more probably, smaller than the virtual level width of the $4f$ state. In the latter case, the Friedel-Anderson model is applicable, since each cell is representative of the whole metal.

The $4f$ level in question is the sixfold-degenerate $J = \frac{5}{2}$ state.[14] The position of this level is assumed to be raised with respect to the Fermi level when the volume of the cell is decreased. In the magnetic β and γ phases the six sublevels are assumed to be split by the intra-atomic Coulomb interaction and exchange, one state lying below and the other five above the Fermi level. With decreasing cell volume, their center of gravity moves upwards with respect to the Fermi level, causing a slight and gradual depopulation of the lowest state. This leads to a slight decrease of the moment on the shell. At the β-α or γ-α phase transition, the $4f$ shell demagnetizes abruptly. (The fact that this transition is of first order at room temperature has been explained with the presence of orbital moment by Coqblin and Blandin.[4])

In the α phase, all six $J = \frac{5}{2}$ sublevels are degenerate and partially filled, resulting in a high density of states at the Fermi level, a large but only weakly temperature-dependent Pauli susceptibility, and a large electronic specific heat, which can be estimated on the basis of this model: Several authors[15] estimate the valence of α-Ce to be ~3.7. Assuming a Lorentzian shape of the $4f$ level and a level half-width of 10^{-2} eV,[12,13] one obtains $\gamma \approx 5$ to 11 mJ/mole °K² for the contribution of the $4f$ level to the electronic specific heat, with 0.2 to 0.3 $4f$ electrons per Ce atom at 10 kbar and 0°K. This is the order of the difference between the electronic specific-heat coefficient measured in α-Ce ($\gamma \approx 10$ mJ/mole °K²) and the four-valent metals like Th ($\gamma = 4.9$ mJ/mole °K²) and Hf ($\gamma = 2.40$ mJ/mole °K²).

The Friedel-Anderson model also makes predictions on the character of the exchange enhancement of α-Ce. As long as there is appreciable local character of the conduction electrons near the Fermi level, i.e., as long as there is appreciable occupancy of the degenerate $4f$ states, there will be intra-atomic Coulomb repulsion, which, although it is no longer able to split the sublevels as in the β and γ phases, will still generate local exchange enhancement. Raising the pressure (or lowering the temperature) results in a further gradual upward shift of the $4f$ level, depopulating it in a continuous manner until its effect, including the exchange enhancement, becomes negligible, i.e., until Ce becomes a truly four-valent metal.

Clearly, the Friedel-Anderson model describes correctly a large part of the observations up to high pressures. However in this model no first-order transition is needed to end up in a superconducting phase. Since such a transition seems to take place near 50 kbar,[16] further experimental studies of Ce in this region will be very interesting, but have to await progress in experimental technique.

---

*Research supported by the U. S. Atomic Energy Commission.

†Research sponsored by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. Af-AFOSR-631-67-A.

[1]J. M. Lock, Proc. Phys. Soc., London: Sect. B 70, 566 (1957).

[2]J. Wittig, Phys. Rev. Lett. 21, 1250 (1968).

[3]J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958); P. W. Anderson, Phys. Rev. 124, 41 (1961).

[4]B. Coqblin and A. Blandin, Advan. Phys. 17, 281

(1968).
[5]D. Wohlleben, thesis, University of California, San Diego, 1968 (unpublished).
[6]A. W. Lawson and T. Y. Tang, Phys. Rev. 76, 301 (1949).
[7]The analysis was performed by Fulmer Technical Services, Stoke Poges, Buckinghamshire, England. The following concentrations were found for the magnetic rare-earth elements (in atomic ppm): Yb 0.3; Tm < 0.03; Er, 4.3; Ho, 1; Dy, 0.5; Tb, 10; Gd, 6.7; Eu < 0.02; Sm < 0.2; Nd, 72; and Pr, 10.
[8]N. E. Phillips, J. C. Ho, and T. F. Smith, Phys. Lett. 27A, 49 (1968); N. T. Panousis and K. A. Gschneidner, Jr., to be published.
[9]T. F. Smith, Phys. Rev. 137, A1435 (1965).
[10]J. Crangle, Phys. Rev. Lett. 13, 569 (1964).
[11]D. Wohlleben, Phys. Rev. Lett. 21, 1343 (1968).
[12]J. G. Huber and M. B. Maple, J. Low-Temp. Phys. 3, 537 (1970), and references cited therein.
[13]K. A. Gschneidner, Jr., in *Rare Earth Research III*, edited by L. Eyring (Gordon and Breach, New York, 1964), based on an optical-absorption experiment by J. F. Wilkins, J. G. Clark, and T. E. Leinhard, Bull. Amer. Phys. Soc. 7, 579 (1962).
[14]Since the virtual level width of about 10^{-2} eV is much smaller than the spin-orbit coupling energy $\xi = 0.3$ eV, the total angular momentum and its z component remain good quantum numbers of the $4f$ shell in the metal.
[15]K. A. Gschneidner, Jr., and R. Smoluchowski, J. Less-Common Metals 5, 374 (1963); E. Franceschi and G. L. Olcese, Phys. Rev. Lett. 22, 1299 (1969).
[16]E. King, J. A. Lee, I, R. Harris, and T. F. Smith, Phys. Rev. B 1, 1380 (1970).

Low-Energy Neutron Energy Spectra from (p, n) Reactions*

B. L. Cohen, J. H. Degnan, C. L. Fink, G. R. Rao, and R. Balasubramanian
University of Pittsburgh, Pittsburgh, Pennsylvania 15213
(Received 12 October 1970; revised manuscript received 20 November 1970)

Coincidence experiments indicate that (p,np) reactions on Zr^{90} and Sn^{112} leave the residual nuclei in their ground states, whence neutron spectra can be deduced from measurements of proton spectra. Results are very different for the two nuclei. Analysis indicates that the variation of σ_i—the cross section for the inverse process—is larger than expected and in opposite directions for the two nuclei.

The measurement of neutron energy spectra in the region below 1 MeV has always been a difficult experimental problem, whence data are generally cut off somewhere above ~0.7 MeV. Unfortunately, the energy region thereby eliminated is one of high interest since it includes the maximum of the distribution and the part of the spectrum with the most rapid energy variation.

In this Letter we report determinations of these spectra by a different technique: measurements of the proton spectrum from (p,np) reactions. If the bombarding energy is below the threshold for $(p,2n)$ but still far above the threshold for (p,np), the latter reaction should result from virtually every (p,n) reaction. If the nucleus formed in the (p,np) reaction is always left in its ground state, there is a one-to-one correspondence between the energies of the emitted neutron E_n and proton E_p since

$$E_n + E_p = E_i + Q + E_r, \tag{1}$$

where E_i and E_r are the incident and recoil energies and Q has its usual meaning. E_r is virtually independent of the angle of neutron emission if E_n is small; hence a measurement of E_p determines E_n. In general this method is not usable since the final nuclei are not left in their ground states, but two nuclides have been encountered in which they are.

The evidence for this is shown in Fig. 1 which was obtained from coincidence detection of the neutrons and protons[1] from (p,np) reactions on Zr^{90} and Sn^{112}. It shows the energy distributions of protons emitted in coincidence with neutrons of various energies, and in both cases there is a strong peak corresponding to the final nucleus being left in its ground state. In the Zr^{90} reaction, the two lowest-energy excited states are $\frac{1}{2}^-$ at 0.6 MeV and $\frac{5}{2}^-$ at 1.1 MeV, and there is no indication that these are appreciably excited. (The counts in this region may be due to scattered neutrons from the ground-state transition.) This is in accordance with expectations since the ground state is $\frac{9}{2}^+$, and there is good theoretical as well as experimental reason to believe that higher angular momentum and lower energy states are preferentially excited.[1] One can therefore be confident that for at least ~1.2 MeV beyond the threshold, there is an accurate correspondence between the proton and neutron energies from (p,np) re-