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Pressure-induced first-order transition associated with $4f$ instability in CeNi

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We present the results of magnetization and resistivity measurements under hydrostatic pressure in the intermediate-valence compound CeNi. We show the existence under pressure of a first-order transition associated with a large decrease of the susceptibility and an increase of the conductivity. This transition is quite analogous to the so-called γ-α transition of cerium metal and is the result of the delocalization of $4f$ electrons induced by pressure. The P-T phase diagram of this transition is determined up to 5 kbar and 150 K. It suggests a critical pressure of ~ 1.3 kbar at $T=0$ between both states.

INTRODUCTION

CeNi crystallizes in the CrB-type orthorhombic structure (space group *Cmcm*). At room pressure this compound exhibits physical properties[1] quite similar to those of $CeSn_3$, which has long been considered as the best example of an intermediate valence system. CeNi behaves as an enhanced Pauli paramagnet in which the magnetic susceptibility, like that of $CeSn_3$,[2,3] passes through a maximum at around 140 K. Moreover, this magnetic susceptibility as well as resistivity and heat-capacity measurements are characteristic of an almost-magnetic Fermi liquid in which spin fluctuations are present.[1] The $4f$ character of the induced magnetization determined from polarized neutron measurements[4] in this low-symmetry compound leads to a strong anisotropy of the magnetic susceptibility.

In systems with unstable $4f$ shells the lattice parameters are strongly related to the intermediate valence character because of the strong electron-lattice coupling, so the elastic properties are of first importance for the understanding of these systems. Magnetostriction measurements[5] in CeNi have shown that volume effects are much larger than in $CeSn_3$. Moreover, a significant softening of the elastic constant C_{11} was observed around 110 K.[6] These properties suggest large pressure effects. In this paper we present the pressure dependence of the magnetic susceptibility and the resistivity of CeNi.

EXPERIMENT

Magnetization and resistivity experiments were performed along **c** and **a** axes on single crystals of CeNi prepared by the Czochralski method. The pressure is applied by means of compressed helium, which allows the production of hydrostatic pressures *in situ* up to 6 kbar at low temperatures. Magnetic fields up to 70 kOe are produced by a superconducting coil. Magnetization is measured by the extraction method. Resistivity measurements were carried out using a four-probe ac technique.

Magnetization along **c** axis in a field of 60 kOe was measured at various pressures (1 bar, 1, 1.6, 2, 3, 4, and 5 kbar) by decreasing and increasing temperature. Results obtained at 3 and 5 kbar are shown in Fig. 1, in comparison with the data obtained at room pressure inside the pressure cell. A drastic drop of the susceptibility takes place around 150 K at 5 kbar and at around 100 K at 3 kbar. It corresponds to a first-order transition with a large hysteresis in temperature ($\simeq 25$–30 K).

In the low-pressure phase when the pressure is increased, we observe an increase in the temperature of the susceptibility maximum and a large decrease in the value of the susceptibility; values are reported in Table I and compared to other intermediate valence compounds. Because the susceptibility of CeNi is anisotropic, we also measured the magnetization of CeNi under pressure along the **a** axis. Figure 2 shows that a first-order transition takes place at 5 kbar at the same temperature along the **a** axis as along the **c** axis.

The transition we show for CeNi is analogous to the γ-α transition found in cerium metal or in $Ce_{0.9}Th_{0.1}$ alloy;[9] it corresponds to a decrease of more than 50% of the bulk susceptibility, which corresponds essentially to the Ce susceptibility in CeNi.[4] The hysteresis in temperature is comparable to that observed in $Ce_{0.9}Th_{0.1}$. To determine the pressure-temperature phase diagram, we have also undertaken magnetization measurements at constant temperature versus increasing and decreasing pressure. Such results are presented in Fig. 3 for two temperatures $T=27$ and 110 K. The first-order transition is still present at 27 K with a large

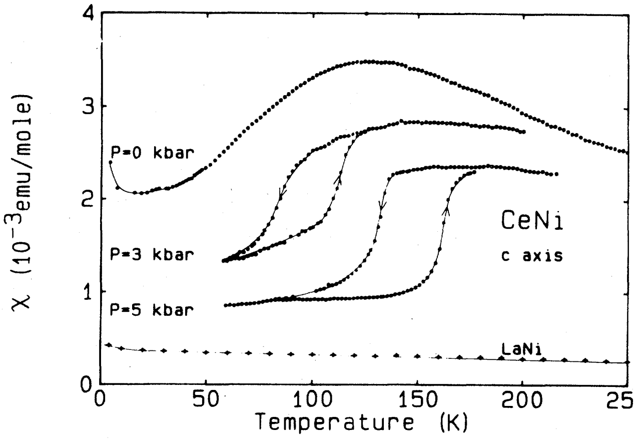

FIG. 1. Thermal variations of the susceptibility of CeNi measured along the **c** axis of the orthorhombic cell at room pressure and under 3 and 5 kbar. Thermal variation of the susceptibility of a polycrystalline sample of LaNi at room pressure.

TABLE I. Comparison of the pressure dependence of the temperature of the susceptibility maximum $T_{\max}$ and of the magnetic susceptibility at 150 and 300 K of some intermetallic Ce compounds.

Sample	$\frac{dT_{\max}}{dP}$ (K kbar^{-1})	$T_{\max}$ at room pressure (K)	$T=150$ K $-\frac{d(\ln\chi)}{dP}$ (10^{-2} kbar^{-1})	$T=300$ K $-\frac{d(\ln\chi)}{dP}$ (10^{-2} kbar^{-1})
CeNi	10.4	140	7.5[a]	$\simeq$ 1.4[a]
$CeSn_3$	3.4 (Ref. 7)	140	1.3 (Ref. 12)	0.7 (Ref. 7) 0.5 (Ref. 13)
$Ce(Rh_{0.7}Pt_{0.3})_2$	3.0 (Ref. 13)	160	1.4 (Ref. 11)	0.6 (Ref. 13)
$CePd_3$	0.65 (Ref. 8)	150		0.4 (Ref. 13)
γ-Ce				1.0 (Ref. 10)

[a] Values obtained from measurements along the **c** axis.

hysteresis with pressure. The pressure hysteresis, which is 1.1 ±0.15 kbar, is to be compared with the one of 2 kbar obtained for the γ-α transition in cerium metal at 300 K.[10] Figure 4 shows the resistivity of a single crystal of CeNi along the **c** axis obtained at 130 K by increasing the pressure up to 6 kbar and then by decreasing the pressure. This indicates that the transition evidenced by magnetization measurements is also associated with a decrease of the resistivity in the high-pressure phase for the α-Ce.

From these data it was possible to determine the pressure-temperature phase diagram of this first-order transition between the two $4f$ electron states. The points which are reported in Fig. 5 correspond to the mean values obtained at constant pressure by increasing or decreasing the temperature or at constant temperature by increasing or decreasing the pressure. To specify this phase diagram, let us mention that thermal variation of the magnetization at 1 and 1.6 kbar does not show any transition down to 4.2 K.

Through the range of temperature and pressure we have investigated the variation of the pressure of the transition is quadratic versus temperature. The extrapolation of the transition line at lower temperatures indicates the existence at $T=0$ K of a critical pressure $[P_c(T=0)\simeq 1.3$ kbar$]$ between the two phases. Effectively, the hysteresis in pressure is as large at 27 K as it is at 110 K, so it seems quite unlikely that the first-order line stops at low temperature as proposed in $Ce_{0.8}Th_{0.1}La_{0.1}$.[11] Unfortunately, due to the solidification phase diagram of helium, it is not possible to vary the pressure at temperatures lower than 27 K.

DISCUSSION

In Ce compounds the main effect of applying pressure is to favor the configuration with smaller volume leading to a delocalization of the $4f$ electron. Therefore, with pressure one expects to observe a decrease of the magnetic susceptibility. Also, the spin-fluctuation temperature, which is a measure of the degree of hybridization between the local moment and the conduction-electron wave functions, should thus increase when pressure is increased. These effects are observed in CeNi as they were previously observed in other intermediate valence systems such as $CeSn_3$,[12,13] $CePd_3$,[13] or $Ce(Rh_{0.7}Pt_{0.3})_2$.[13] Indeed, at any temperature one observes a decrease of the magnetic susceptibiilty and an increase of the temperature of its maximum, which can be taken as a rough measure of the fluctuation temperature.

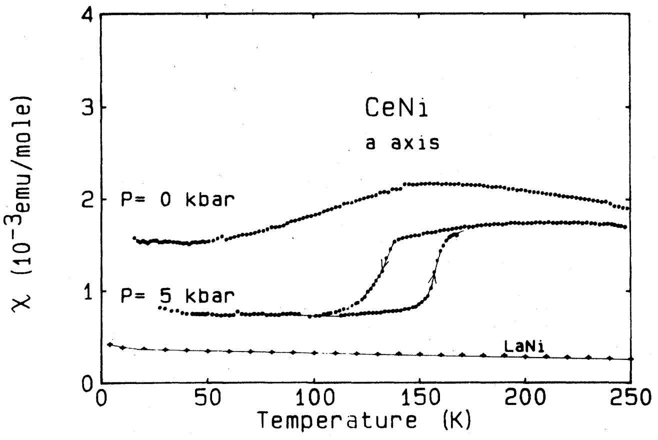

FIG. 2. Thermal variations of the susceptibility of CeNi measured along the **a** axis of the orthorhombic cell at room pressure and under 5 kbar. Thermal variation of the susceptibility of a polycrystalline sample of LaNi at room pressure.

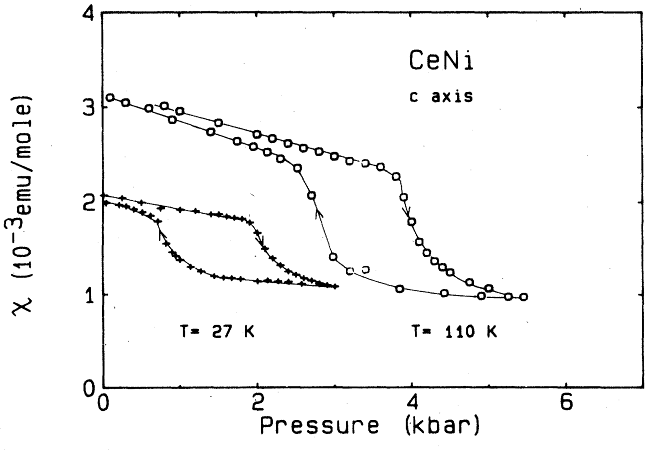

FIG. 3. Pressure dependences of the susceptibility of CeNi measured along the **c** axis at 27 and 110 K.

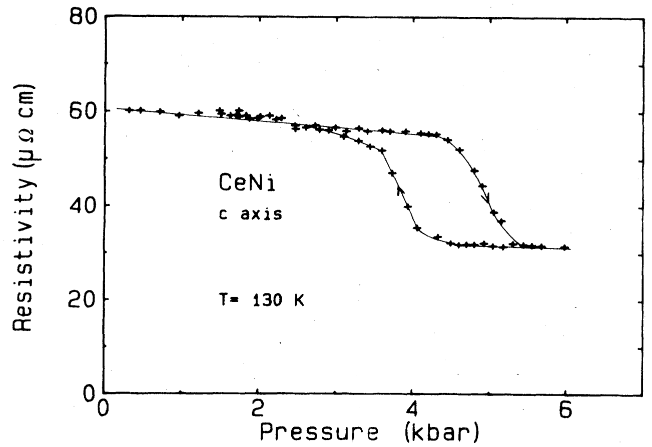

FIG. 4. Pressure dependence of the resistivity of CeNi measured along the c axis at 130 K.

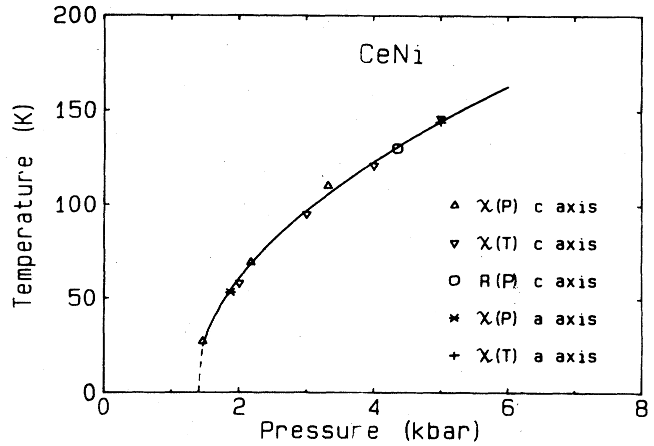

FIG. 5. *T-P* diagram of the low and high magnetic states in CeNi.

In CeNi, as in the above-mentioned materials, for small pressure the pressure dependence of the magnetic susceptibility $|d(\ln\chi)/dP|$ strongly increases with decreasing temperature, but saturates for temperatures smaller than the fluctuation temperature.

However, pressure effects are quantitatively much higher in CeNi than in $CeSn_3$, $CePd_3$, and $Ce(Rh_{0.7}Pt_{0.3})_2$. This is illustrated in Table I, where we have compared dT_{max}/dP and $d(\ln\chi)/dP$ at room temperature and at 150 K, which for all these compounds is very close to the temperature of the susceptibility maximum. Especially at 300 K the value of $d(\ln\chi)/dP$ for CeNi is more comparable to that of γ-Ce.[10] In CeNi the 4*f* instability is so high that pressure induces a transition between a high and a low magnetic state of the 4*f* electrons. As in pure Ce, this transition, in the temperature and pressure range that we have investigated, is of first order. In the high-pressure phase and under 5 kbar, which is the maximum pressure we have applied, we still observe 4*f* magnetism. Indeed, the susceptibility is higher than in the LaNi reference compound; moreover, the anisotropy of the susceptibility between the **a** and **c** axes, although smaller than in the low-pressure phase, is still present.

As in pure Ce, in CeNi it is not possible to conclude if the driving forces behind the γ-α Ce-like transition correspond to the promotion model proposed by Coqblin and Blandin[14] or to the Kondo collapse as proposed more recently by Lavagna, Lacroix, and Cyrot[15] and by Allen and Martin.[16] Indeed, the decrease of the resistivity, and especially its drop at the transition, is expected in both models. In the first one it is simply a consequence of the delocalization of the 4*f* shell leading to an increase of the number of conduction electrons. In the second one the decrease of the resistivity is a consequence of the decrease of the effective mass of the conduction electron associated with the increase of the Kondo temperature.

Further investigations on such things as lattice parameters and the resistivity and susceptibility at higher pressures than 5 kbar are in progress so that we may learn more about the *P-T* phase diagram of CeNi. We especially hope to observe the high-pressure critical point.

In conclusion, we have given evidence for the existence of a pressure-induced first-order transition in CeNi between two different 4*f* electronic states and established its *P-T* phase diagram.

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