

Pressure-dependent magnetism and electrical resistivity of $\text{UFe}_4\text{P}_{12}$

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$\text{UFe}_4\text{P}_{12}$ is the first reported uranium-based ferromagnetic semiconductor. The Curie temperature T_C is 3.15 K, and the spontaneous magnetic moment σ_0 which at $T = 1.14$ K was found to be $\approx 1.0 \mu_B/(\text{U atom})$, is associated entirely with the uranium ions. The electrical resistivity $\rho(T)$ increases by nearly 7 orders of magnitude as temperature is decreased from room temperature to 4.2 K. The behavior of the ferromagnetic and electrical properties of $\text{UFe}_4\text{P}_{12}$ in hydrostatic pressures up to 16 kbar is reported. Quasihydrostatic-pressure effects on $\rho(T)$ to 100 kbar are also reported. Although T_C increases sharply with increasing pressure at the rate $dT_C/dP = 0.26$ K/kbar (in contrast to similar data on the isomorphous ferromagnet $\text{NdFe}_4\text{P}_{12}$, where $dT_C/dP = 0.03$ K/kbar), σ_0 decreases, $(1/\sigma_0)(d\sigma_0/dP) = -0.007$ kbar⁻¹. Hydrostatic and quasihydrostatic pressure have little effect on $\rho(T)$.

INTRODUCTION

Experiments conducted at high hydrostatic pressure on systems with unstable magnetic moments can reveal important details of the electronic interactions leading to magnetic-moment formation. For metallic systems where the interaction between stable localized moments is dominated by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, i.e., where Kondo or intermediate-valence effects are weak, the Néel or Curie temperatures, T_N or T_C , respectively, are proportional to $J^2 N(E_F)$, where J is the damped oscillatory exchange interaction strength and $N(E_F)$ is the density of states at the Fermi surface. The pressure dependences of T_N or T_C in these cases in metallic systems are generally fairly weak and with a sign which depends on the relative magnetic-moment position in the damped oscillatory RKKY exchange field.¹ For somewhat less stable moment systems where the f level ($4f$ in the case of rare-earth metals or $5f$ for the actinides) is near the Fermi level, the intra-atomic Coulomb interaction, which favors moment formation, may compete with the Kondo effect, in which the moment tends to be screened by the conduction electrons. In this case pressure may first cause an increase, then eventually a decrease in T_N or T_C .¹ The Kondo temperature T_K , which characterizes the strength of the Kondo effect, tends to increase with increasing pressure.² The application of pressure can, in principle, be used to sweep unstable moment systems conveniently from one extreme to the other, from RKKY-dominated to Kondo-dominated behavior.

The largest body of high-pressure experimental work showing these effects has been carried out on compounds and alloys where the magnetically active components are

the light actinides or some of the light rare-earth metals. Few of the many binary or ternary rare-earth-metal- and actinide-based intermetallic compound systems have as wide a range of low-temperature physical properties as the class of compounds having the bcc $M\text{Fe}_4\text{P}_{12}$ structure, where M is a light rare-earth metal, thorium, or uranium. The $M\text{Fe}_4\text{P}_{12}$ compounds show metallic conductivity ($d\rho/dT > 0$) with the exception of $\text{CeFe}_4\text{P}_{12}$ and $\text{UFe}_4\text{P}_{12}$,³ which are semiconductors. $\text{LaFe}_4\text{P}_{12}$ becomes superconducting below 4.1 K,⁴ and Mössbauer-effect measurements⁵ show negligible magnetic moment on the Fe sites. We infer negligible moment on the Fe sites in the other isomorphous $M\text{Fe}_4\text{P}_{12}$ systems. Consequently, the magnetic properties of the $M\text{Fe}_4\text{P}_{12}$ compounds are governed by magnetic-moment formation on the M sites. In this report we focus on the results for what is perhaps the most intriguing of them, namely $\text{UFe}_4\text{P}_{12}$. Specific-heat and magnetic measurements at ambient pressure verify that $\text{UFe}_4\text{P}_{12}$ becomes ferromagnetic at $T_C = 3.2$ K and that this is a bulk transition, having a magnetic entropy of about $1.3k_B \ln 2$.³ The resistivity near T_C is nearly 7 orders of magnitude larger than that near room temperature (about $1000 \mu\Omega \text{ cm}$), and a large negative magnetoresistance near T_C was also found for $\text{UFe}_4\text{P}_{12}$.³ $\text{UFe}_4\text{P}_{12}$ is one of the relatively small class of ferromagnetic semiconductors. EuO and EuS (Ref. 6) are the most studied ferromagnetic semiconductors, and among the others are included CrBr_3 (Ref. 7) and HgCr_2Se_4 (Ref. 8). However, $\text{UFe}_4\text{P}_{12}$ is the first one with a regular periodic actinide sublattice. Given the enormously high electrical resistivity of $\text{UFe}_4\text{P}_{12}$ in the region of the ferromagnetic transition, the U-U coupling responsible for the ordered state probably comes from a superexchange mechanism.⁶

In this paper we present the results of high- and low-field magnetization measurements at temperatures near T_C , both at ambient and at high hydrostatic pressures to 11 kbar. The results of electrical-resistivity measurements are also presented, also at ambient and at hydrostatic pressures to 15 kbar, and in quasihydrostatic pressures to 108 kbar. The results indicate a rapid increase in T_C but little change in the resistivity under pressure.

EXPERIMENTAL DETAILS

In this study the $\text{UFe}_4\text{P}_{12}$ samples used were rectangularly shaped single crystals grown in Sn flux. The methods used to make the measurements of magnetization at high pressure have been described elsewhere.⁹ Resistivity measurements at high pressure were performed using beryllium-copper self-locking pressure-clamp devices with electric-lead access through an epoxy seal into the high-pressure chamber. Gold-filled epoxy was used to attach leads to the sample, which was first sand blasted in order to roughen the otherwise very smooth surface.

RESULTS AND DISCUSSION

In Fig. 1 we show the magnetization σ in fields H to 10 T for $T=4.2$ and 1.6 K, the latter being below T_C . The data for Fig. 1 were taken with the magnetic field applied along the long axis of the rectangularly shaped samples, although the approach to saturation did not seem to be orientation dependent. The spontaneous magnetization σ_0 is clearly observable for $T < T_C$, and a plot of σ_0 versus T is shown in the inset of Fig. 1. The magnetization was also measured at the same two temperatures to 23 T, using Bitter solenoids of the Francis Bitter National Magnet Laboratory (data not shown). Magnetic saturation was finally reached at $H > 15$ T and was about $1.3 \mu_B/(\text{U atom})$, which is typical for magnetic saturation in U-based systems.¹⁰ Arrott-plot (σ^2 versus H/σ) analysis (not shown) was also carried out on $\text{UFe}_4\text{P}_{12}$, and the T_C so determined ($T_C = 3.0 \pm 0.3$ K) agreed well with the specific-heat results as well as the low-field magnetization results, discussed below.

In Fig. 2 we show plots of σ versus T taken at very low applied magnetic fields $H < 50$ G (0.005 T) at temperatures near T_C and at three hydrostatic pressures up to 11.3 kbar. This "kink-point" method of determining the onset of ferromagnetism is associated with the rapid rise in σ near T_C in very low measuring fields.¹¹ The value of σ in highly permeable systems rises to a limit determined by the demagnetizing factor of the sample. (Note that for $H=20$ G, T_C determined in this way is the same as for $H=50$ G. This proves that the 50 G measuring field is sufficiently low for determination of T_C with the kink-point method.) A large increase in T_C with increasing pressure is seen; $dT_C/dP \approx 0.26$ K/kbar, and this is depicted in the inset of Fig. 2. Since the transition to the ferromagnetic state was accompanied by a large and rather sharp maximum in the ac susceptibility χ_{ac} , the pressure dependence of T_C was also measured using low-frequency (16 Hz) χ_{ac} measurements. The peak in χ_{ac} broadened considerably and decreased in

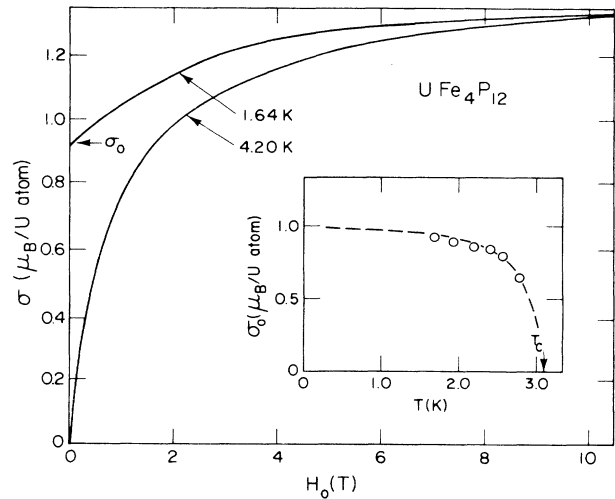


FIG. 1. Magnetization of $\text{UFe}_4\text{P}_{12}$ in fields to 10 T for $T=4.20$ and 1.64 K. The Curie temperature of $\text{UFe}_4\text{P}_{12}$ is 3.15 K. The spontaneous moment vs T is shown in the inset.

magnitude under pressure, and the dT_C/dP determined this way was smaller than the increase determined with the kink-point method. (The full width at half maximum of χ_{ac} in the region of the ferromagnetic transition broadened from 0.5 to 1.5 K by 10 kbar. However, this broadening cannot be attributed to nonhydrostaticity in the pressure cell, because there was no concomitant broadening of the superconducting transition temperature of the Pb manometer, also in the high-pressure region of the cell.) If the leading edge of the ac-susceptibility maximum is used, the agreement between the two methods (χ_{ac} and σ_{ac}) is quite good. This points out a difficulty in using ac susceptibility for accurate determination of Curie temperatures or their pressure dependence. To put into perspective the large increase of T_C with pressure for $\text{UFe}_4\text{P}_{12}$, we measured the pressure dependence of the Curie temperature for the isomorphous metallic ferromagnet $\text{NdFe}_4\text{P}_{12}$ ($T_C=2.0$ K),

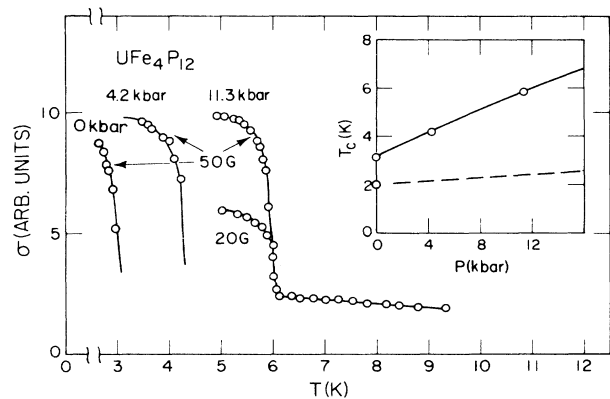


FIG. 2. The low-field magnetization of $\text{UFe}_4\text{P}_{12}$, vs T for three hydrostatic pressures. Data at 50 and 20 G show the same Curie temperature T_C for $P=11.3$ kbar. The inset shows the increase of T_C vs P (solid line), and the dashed line shows the much weaker dependence on P of T_C for the isomorphous ferromagnetic, $\text{NdFe}_4\text{P}_{12}$ ($T_C=2.0$ K for $P=0$ kbar).

which did not broaden with pressure. We found $dT_C/dP \approx 0.03$ K/kbar (see Fig. 2), compared $dT_C/dP \approx 0.26$ K/kbar for $\text{UFe}_4\text{P}_{12}$.

The rather strong broadening effect of pressure for χ_{ac} suggests a possible reduction in the U magnetic moment with increasing pressure, or possibly a change in the coupling strength between the U atoms. In order to test this directly, we measured the field dependence of the magnetization for $T < T_C$ at several pressures as shown in Fig. 3. In contrast to the case of T_C , σ_0 actually decreases with increasing pressure, as indicated in the inset of Fig. 3. The crossover of the σ -versus- H data for $P=0$ data with the data for $P=11$ kbar at 0.8 T is not well understood. Pressure-dependent magnetic studies of the metallic ferromagnet UPt show similar results, although in that case T_C remained relatively constant as σ_0 decreased sharply with increasing pressure.¹² For $\text{UFe}_4\text{P}_{12}$ the results could be explained by a pressure-induced change in the crystalline electric field,¹³ but it is more likely an indication of a weakening of the magnetic moment with increased hybridization of the f -shell-electron wave functions with the wave functions of the more itinerant electrons of the system, perhaps the Fe d electrons. The rapid increase in T_C with pressure is difficult to understand in this picture unless this is only the initial increase in T_C expected in models involving the competition between the Kondo-effect and RKKY-dominated mechanisms,¹⁴ alluded to above. If this were

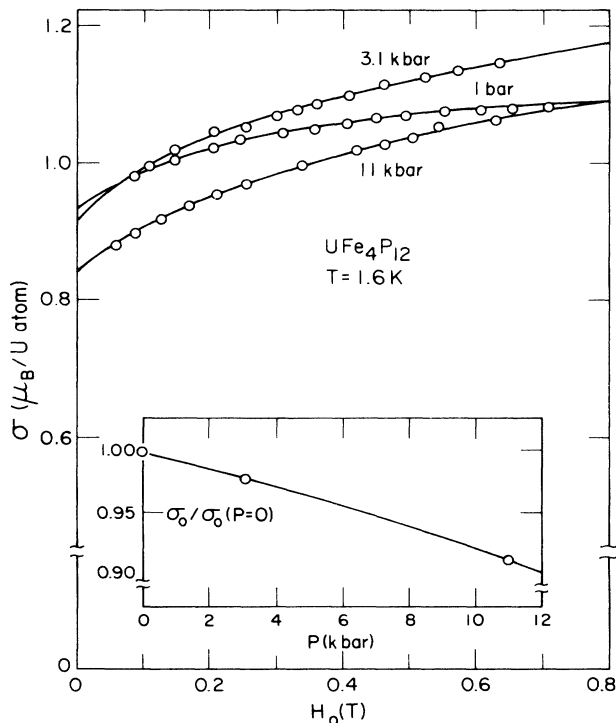


FIG. 3. Magnetization of $\text{UFe}_4\text{P}_{12}$ to 0.8 T for three pressures at $T = 1.6$ K, which is below the Curie temperature. The crossover at low fields between the 1-bar and 3.1-kbar data is reproducible. The inset shows the decrease with increasing pressure of the spontaneous moment σ_0 .

the case, namely that the Kondo effect plays a role in the determination of T_C , then T_C should ultimately decrease again at high pressures because the moment will eventually be quenched in the extreme Kondo limit. (The observed decrease in σ_0 with increasing pressure may be a precursor of this Kondo-dominated effect.)

As mentioned above, the temperature dependence of the electrical resistivity, $\rho(T)$, demonstrates both $\text{CeFe}_4\text{P}_{12}$ and $\text{UFe}_4\text{P}_{12}$ to be semiconductors. As with all semiconducting systems, there is some variability from sample to sample of the absolute value of $\rho(T)$. However, the salient features of the temperature dependence are quite consistent, with six samples having been tested, three rectangular and three cubic shaped. The resistivity increased monotonically with decreasing temperature, with a slight knee at about 100 K and with a rather abrupt increase at about 20 K. Finally, the resistivity ratio, $R(4 \text{ K})/R(300 \text{ K})$ is nearly 10^7 . No single excitation energy can be ascribed to $\rho(T)$ over the entire temperature range, nor does hopping conductivity account for the observed behavior [plots of $\ln(\rho)$ versus $T_{-1/4}$ did not yield straight lines]. $d\rho/dT$ is so large and negative near T_C it is difficult to see if any anomaly in $\rho(T)$, such as spin-disorder resistivity, accompanies the transition to the ferromagnetic state. If the coupling between U atoms that is responsible for the $\text{UFe}_4\text{P}_{12}$ ferromagnetism is mediated by conduction electrons, their mobility must be very low.

The slight decrease in σ_0 with increasing pressure (shown in Fig. 3) suggests that pressure may increase U f -shell hybridization with more itinerant, say d , electrons, and it follows that some increase in electrical conductivity might accompany this increased hybridization. Therefore, we have measured the pressure dependence of $\rho(T)$ for several hydrostatic pressures up to 16 kbar. However, no substantial decrease in resistivity is observed, as can be seen from the data in Fig. 4, where $\rho(T)$ versus T is shown for $P=0$ and at one representative high pressure, $P=16$ kbar. This is surprising, given the rather substantial effect of pressure on the magnetism of $\text{UFe}_4\text{P}_{12}$, so we conclude that the magnetic and electrical properties of $\text{UFe}_4\text{P}_{12}$ are somewhat decoupled, at least up to hydrostatic pressures of about 20 kbar. A

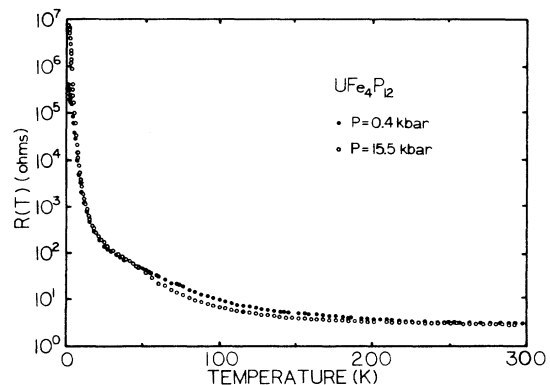


FIG. 4. Electrical resistivity $\rho(T)$ of $\text{UFe}_4\text{P}_{12}$ for two hydrostatic pressures, $P = 0$ and 15.5 kbar.

superexchange mechanism is presumably responsible for the U-U coupling in $\text{UFe}_4\text{P}_{12}$, and the pressure dependence could depend on a number of factors including intra-atomic f - d overlap and the energy difference between a $5f$ electron and nearest-neighbor d electrons.⁶

Using two quite different self-locking pressure-clamp devices with opposed tungsten carbide anvils, we measured $\rho(T)$ for $2 < T < 300$ K in quasihydrostatic pressures up to 108_{-25}^{+10} kbar. Pressure was determined with a superconducting Pb manometer which was included in the high-pressure-cell region (about 2 mm square). The position and width of the superconducting transition temperature for Pb is a measure of pressure magnitude and its hydrostaticity for the cell at low temperatures. One set of measurements of $\rho(T)$ in quasihydrostatic pressures up to 108 kbar indicated the occurrence of metallic behavior and superconductivity with a superconducting transition temperature of about 3 K. It was determined that the Pb was not responsible for this behavior by measuring $\rho(T)$ without the Pb manometer in place. The metallic-superconducting behavior, however, could not be reproduced in two other independent runs, where pressures up to 100 kbar were found to produce almost no changes in $\rho(T)$ for $2 < T < 300$ K. In one of the independent runs the sample was allowed to crack under the stress of the clamp pressure and in the other independent run it was first powdered before putting it in the clamp (which was the procedure used in the case where superconductivity was observed). It is possible that the metallic behavior observed in the first run was due to a disproportionation phenomenon or more likely to filamentary conductivity of residual Sn flux,¹⁵ which could have remained attached to voids on the surface. Another origin of superconductivity could be the presence in the crystal of small inclusions of U_6Fe , which is known to be superconducting below 3.9 K with a rather small sensitivity to applied pressure.¹⁶

Because there appears to be no anomaly in the electrical resistivity data at the Curie temperature of $\text{UFe}_4\text{P}_{12}$, the participation of conduction electrons in the U-U coupling process is unlikely. Thus in the ferromagnetic semiconducting state the uranium ions couple ferromagnetically through a superexchange mechanism. If a hybridization¹⁷ gap is responsible for the semiconducting behavior of $\text{UFe}_4\text{P}_{12}$, it would be interesting to try to understand the relationship between this gap and the localized f -shell-electron coupling. The study of actinide magnetism is a very active one at present, with uranium-based compounds and alloys providing the richest variety of magnetic and superconducting phenomena. The addition of uranium-based semiconducting ferromagnetism to the list of properties is an important one. Future studies should focus a search for other actinide semiconducting systems that are ferromagnetically ordered and on trying to understand the superexchange mechanism responsible for actinide magnetic coupling.

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