PHYSICAL REVIEW B VOLUME 36, NUMBER 16 1 DECEMBER 1987

Low-temperature properties of rare-earth and actinide iron phosphide compounds MFe_4P_{12} (M = La, Pr, Nd, and Th)

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(Received 14 July 1987)

The low-temperature properties of MFe_4P_{12} (M = La, Pr, Nd, and Th) single crystals have been studied by means of electrical-resistivity, magnetization, specific-heat, and magnetoresistivity measurements. Superconductivity among these compounds is known to occur only in $LaFe_4P_{12}$, which has a superconducting transition temperature T_c of $\sim$4 K. The compounds $PrFe_4P_{12}$ and $NdFe_4P_{12}$ display features that suggest the occurrence of antiferromagnetic ordering below $\sim$6.2 K and ferromagnetic ordering below $\sim$2 K, respectively. Isothermal magnetization curves for $PrFe_4P_{12}$ below 6 K reveal a spin-flop or metamagnetic transition.

INTRODUCTION

A series of rare-earth (R) ternary phosphides with general formula RT_4P_{12} (T = Fe, Ru, and Os; R = La, Ce, Pr, Nd, Sm, and Eu) has been reported to form in a bcc crystallographic structure by Jeitschko and Braun.[1] This structure is derived from the $CoAs_3$- and WAl_{12}-type structures by filling the icosahedral and octahedral voids with R and T atoms, respectively.[1] Later, compounds with the actinides Th (Ref. 2) and U (Ref. 3) at the rare-earth sites were found to form with the same structure.

One of the most striking features of these compounds was discovered by Meisner,[4] who reported the occurrence of superconductivity in $LaFe_4P_{12}$ with a superconducting transition temperature T_c onset of 4.08 K. Together with RFe_3Si_5 [R = Sc, Y, and Lu (Ref. 5)], U_6Fe (Ref. 6), Fe_3Th_7 (Ref. 7), and $FeZr_2$ (Ref. 8), $LaFe_4P_{12}$ is one of the few Fe compounds ever found to exhibit superconductivity. Superconductivity has also been observed in the compounds $LaRu_4P_{12}$ (Ref. 4) and $LaOs_4P_{12}$ (Ref. 9) with onsets at 7.02 K and 1.83 K, respectively. Mössbauer-effect measurements on $LaFe_4P_{12}$ (Ref. 10) revealed a very small upper limit of $0.01\mu_B$ for the magnetic moment of the Fe ions in this compound, which is consistent with the occurrence of superconductivity, in spite of the large Fe concentration of $\sim$24 at. %. A moderately high electronic specific-heat coefficient $\gamma = 57$ mJ/mole K^2 and a specific-heat jump at T_c equal to $\sim$87% of that expected from the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity was derived from specific-heat, C, measurements[11] on $LaFe_4P_{12}$. The latter result indicates that superconductivity in $LaFe_4P_{12}$ is a bulk phenomenon.

Electrical-resistivity, ρ, and dc-magnetic-susceptibility, χ, measurements on other MFe_4P_{12} (M denotes rare earth or actinide) compounds yield certain anomalies that can be associated with magnetic ordering or f-electron hybridization.[12–14] The compounds $CeFe_4P_{12}$ (Refs. 12 and 13) and UFe_4P_{12} (Ref. 3) exhibit nonmetallic behavior in which the value of the resistivity at low temperatures is 6–7 orders of magnitude larger than the value at room temperature. However, the magnetic properties of $CeFe_4P_{12}$ and UFe_4P_{12} are substantially different from one another. While UFe_4P_{12} is ferromagnetic with a Curie temperature of 3.15 K, the magnetic susceptibility of $CeFe_4P_{12}$ can be described by an enhanced Pauli-like susceptibility plus a Curie term, which can be accounted for by $\sim$0.3% Ce^{3+} ions per formula unit.[3] The compounds $PrFe_4P_{12}$ (Ref. 12), $NdFe_4P_{12}$ (Ref. 14), $EuFe_4P_{12}$ (Ref. 13), and $ThFe_4P_{12}$ show metallic behavior, and curves of $\rho(T)$ for the first three of them contain anomalies that are associated with the occurrence of magnetic ordering.

Reported herein are the results of an investigation that consisted of measurements of electrical resistivity in zero and applied magnetic fields, ac and dc magnetization, and specific heat on the MFe_4P_{12} compounds with M = La, Pr, Nd, and Th. The magnetic properties of $CeFe_4P_{12}$ and UFe_4P_{12} (Ref. 15), the properties of UFe_4P_{12} under high pressure,[16] and a crystalline-electric-field analysis of the magnetic susceptibility of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ (Ref. 17) are the subjects of forthcoming publications.

EXPERIMENTAL DETAILS

Single crystals of MFe_4P_{12} compounds were grown in a molten Sn flux. High-purity (99.9% or better) pieces of the M elements (La, Pr, Nd, and Th), Fe, P, and Sn were placed in a quartz tube in the proportions of 1:4:20:50 and sealed off under 150 mm Hg of argon gas.

The quartz tube was placed in a furnace and the temperature was elevated to 1050–1150 °C. The quartz tube was maintained at this temperature for about a week, and the temperature was then decreased at the rate of 2 °C/h. When the temperature of the furnace reached about 600 °C, the quartz tube was dropped into water, and the product of the reaction, consisting of several single crystals embedded in the Sn-P solution, was recovered. These single crystals, with typical dimensions somewhat less than 2 mm, could be isolated after dissolving the Sn-P matrix with a concentrated solution of HCl, which took several hours. The crystal structure of a few of these crystals was verified utilizing a Gandolphi x-ray camera.

Copper or platinum leads were attached to the samples with silver-filled epoxy, and four-lead electrical-resistivity measurements were performed using a self-balancing impedance bridge operating at a frequency of 16 Hz. The magnetic-susceptibility measurements and the magnetization curves on $PrFe_4P_{12}$ were obtained utilizing a S.H.E. Corp. superconducting quantum-interference device (SQUID) susceptometer, while the magnetization curves for $NdFe_4P_{12}$ were obtained with a vibrating-sample magnetometer.

For the specific-heat measurements, several single crystals of each compound weighing ~ 0.5 g were placed in a copper container with Crycon grease to provide good thermal conductivity between the crystals.[18] Specific-heat measurements above 0.5 K were performed in a ^{3}He semiadiabatic calorimeter using a heat-pulse technique.

RESULTS AND DISCUSSION

Electrical resistivity normalized to room-temperature $\rho/\rho_{300\,\mathrm{K}}$ versus temperature data for $LaFe_4P_{12}$, $PrFe_4P_{12}$, $NdFe_4P_{12}$, and $ThFe_4P_{12}$ are displayed in Figs. 1(a)–1(d) and reveal a positive temperature dependence, like in typical metals. The very large residual resistivity ratio (RRR) of ~ 90 for $LaFe_4P_{12}$ indicates that the Sn-grown single crystals are of very good metallurgical quality. The superconducting transition of $LaFe_4P_{12}$ at ~ 4 K is shown in the inset of Fig. 1(a). As the temperature is lowered, $\rho(T)$ for $PrFe_4P_{12}$ increases sharply at ~ 6.2 K, a temperature at which a cusp in the χ^{-1}-versus-T data and a large peak in the C-versus-T data are observed (see below). Since no significant changes in the x-ray powder-diffraction pattern of $PrFe_4P_{12}$ were detected down to 4 K, the possibility that the anomalies observed in the $\rho(T)$, $\chi(T)$, and $C(T)$ data are due to a crystallographic phase transformation can be ruled out, and the features can more likely be attributed to the onset of antiferromagnetic ordering, as will be discussed below. Below 6 K, $\rho(T)$ exhibits a maximum at ~ 5 K and an abrupt change in slope at ~ 2.5 K. The detailed behavior of $\rho(T)$ for $T < 2.5$ K is somewhat sample dependent, while the sharp increase at ~ 6.2 K is not. The $\rho(T)$ curve for $NdFe_4P_{12}$ shows a broad minimum near 33 K, followed by a sharp drop at ~ 2 K, which is associated with the onset of magnetic ordering. For $ThFe_4P_{12}$, $\rho(T)$ displays a monotonic metallic behavior, with much greater scattering the (RRR is much smaller) than for $LaFe_4P_{12}$, while no superconductivity was found down to 1.2 K (Fig. 1).

Measurements[9] (not shown) of ac magnetic susceptibility χ_{ac} on these compounds have revealed interesting features that can be associated with their superconducting or magnetically ordered states. As expected, there is a sharp drop in $\chi_{ac}(T)$ at T_c for $LaFe_4P_{12}$, and a pronounced peak in $\chi_{ac}(T)$ at 2 K is observed for $NdFe_4P_{12}$, which is consistent with the occurrence of magnetic ordering, while a small peak in $\chi_{ac}(T)$ near 6 K is observed for $PrFe_4P_{12}$.

Plots of χ^{-1} versus T between 2 and 300 K for $PrFe_4P_{12}$ and $NdFe_4P_{12}$ are shown in Figs. 2(a) and 2(b). Since the M-versus-H curves to $H = 1$ T are nearly linear in this temperature range [see Figs. 3(a) and 3(b)], the χ^{-1} values in Fig. 2 were taken from H/M values at 1 T. The feature at ~ 6.2 K in $PrFe_4P_{12}$ suggests the occurrence of antiferromagnetic ordering below this temperature. The linear slope of χ^{-1} versus T from 80 to 300 K yields an effective magnetic moment μ_{eff} of $\sim 3.62\mu_B$, very close to the Pr^{3+} free-ion value of $3.58\mu_B$. The effective moment obtained from the slope below 40 K is $\mu_{\mathrm{eff}} \sim 3.18\mu_B$. The difference between the values of μ_{eff} estimated from the χ^{-1}-versus-T data below 40 K and above 80 K indicates that crystalline electric fields are important in determining the magnetic properties of this compound. The linear slope of χ^{-1} versus T from 180 to 300 K in $NdFe_4P_{12}$ corresponds to an effective moment of $\sim 3.53\mu_B$, close to the Nd^{3+} free-ion value of $3.62\mu_B$. The value of μ_{eff} obtained from the slope at low temperatures yields $\mu_{\mathrm{eff}} \sim 2.46\mu_B$. As in $PrFe_4P_{12}$, the difference in the values of μ_{eff} inferred from the slopes of χ^{-1} versus T at high and low temperatures, as well as the slight positive departure from the linear behavior near 150 K, suggests the occurrence of crystalline-electric-field effects in $NdFe_4P_{12}$. Magnetic-susceptibility measurements performed with a Faraday magnetometer on different batches of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ (Refs. 9 and 17) yielded $\chi^{-1}(T)$ plots very similar to the ones shown in Fig. 2, with slight discrepancies in the higher-temperature range, where the μ_{eff} values obtained were $3.64\mu_B$ and $3.86\mu_B$, respectively.

Further evidence for antiferromagnetic ordering in $PrFe_4P_{12}$ is provided by the isothermal magnetization curves shown in Fig. 3(a). For $T = 3$ and 4 K, a magnetic-field-induced transition is seen, characteristic of either a spin-flop or metamagnetic transition. The magnetization curve for $PrFe_4P_{12}$ [Fig. 3(a)] at 3 K yields a saturation value at 5 T of $\sim 1.58\mu_B$/Pr ion, much less than the Pr^{3+} free-ion value of $3.2\mu_B$/Pr ion. Further experiments will be carried out to determine the field-temperature magnetic phase diagram for $PrFe_4P_{12}$ and identify the magnetic phases. Magnetization measurements were performed on $NdFe_4P_{12}$ at $T = 1.4$ and 4.2 K in fields to 5 T [Fig. 3(b)]. The magnetization at 1.4 K saturates in a field of 5 T to $\sim 1.72\mu_B$/Nd ion, to be compared with the Hund's-rule value of $3.27\mu_B$. Only very small hysteresis was detected at 1.4 K, which

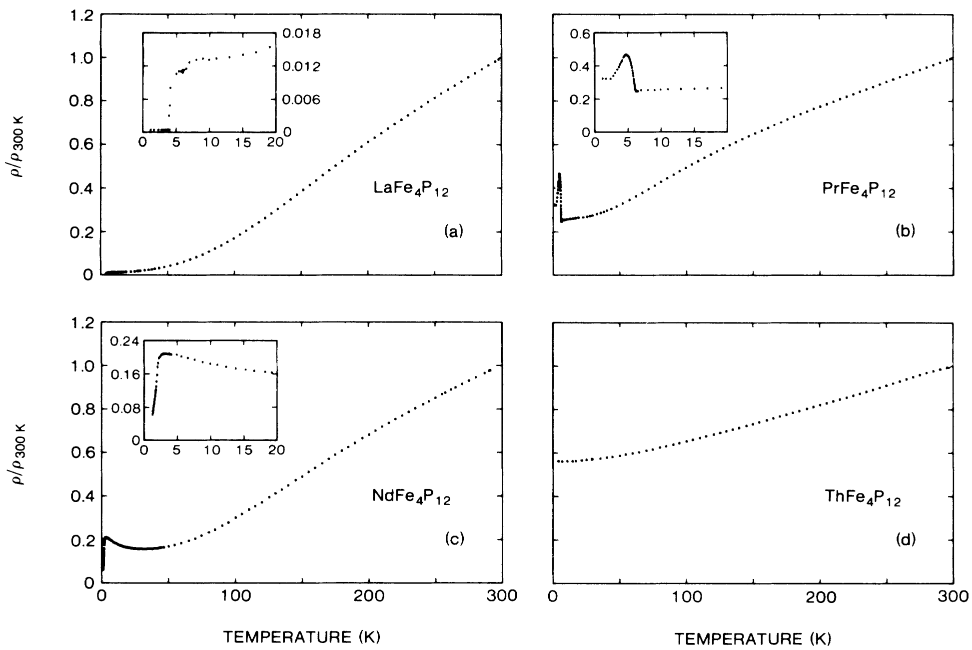

FIG. 1. Normalized electrical-resistivity $\rho/\rho_{300\ K}$ vs temperature for (a) $LaFe_4P_{12}$, (b) $PrFe_4P_{12}$, (c) $NdFe_4P_{12}$ and (d) $ThFe_4P_{12}$.

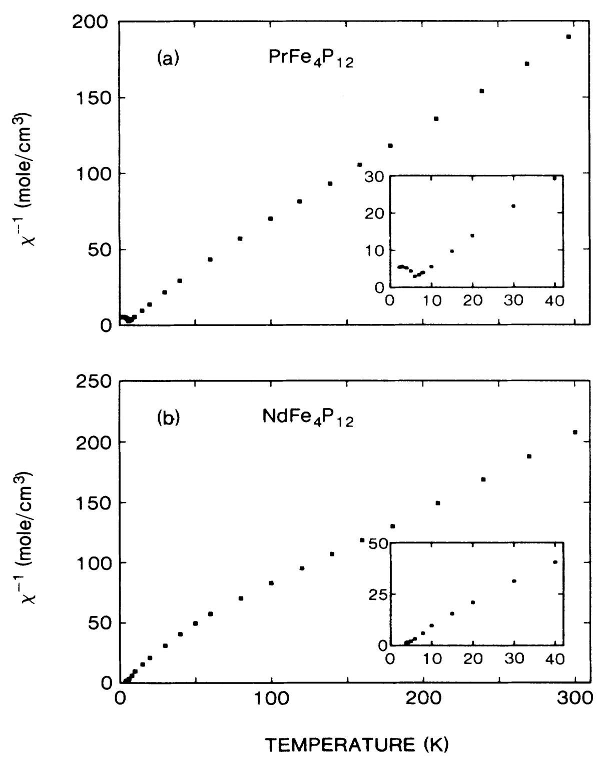

FIG. 2. Inverse magnetic susceptibility χ^{-1} vs temperature for (a) $PrFe_4P_{12}$ and (b) $NdFe_4P_{12}$.

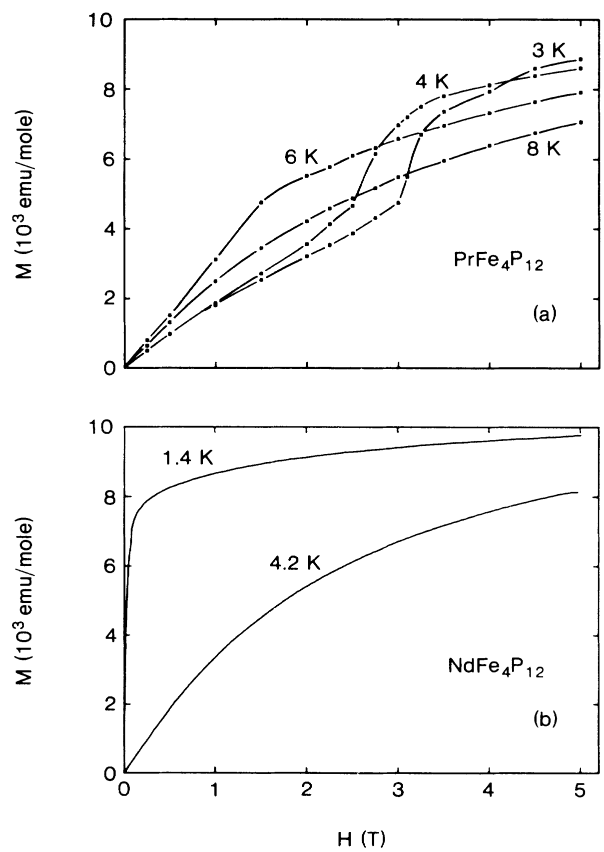

FIG. 3. Isothermal magnetization curves for (a) $PrFe_4P_{12}$ and (b) $NdFe_4P_{12}$. Solid lines in (a) are guides to the eye.

reveals that the coercivity of $NdFe_4P_{12}$ is small.

Specific-heat, C, versus temperature data for $PrFe_4P_{12}$ and $NdFe_4P_{12}$ are displayed in Fig. 4. These data reveal very pronounced peaks at the magnetic ordering temperatures T_M. The contribution of the lattice to the specific heat below T_M can be estimated from the C-versus-T data for $LaFe_4P_{12}$ (Ref. 11) and is small enough compared to the magnetic contribution to be neglected at these temperatures. The peak in $C(T)$ at ~ 6 K for $PrFe_4P_{12}$ correlates well in temperature with the sharp increase in $\rho(T)$, and with the feature in $\chi^{-1}(T)$. No signature of the feature in $\rho(T)$ below ~ 3 K is seen in the $C(T)$ data. The behavior of $C(T)$ below T_M can be described reasonably well by a $T^{3.1}$ law ($C \propto T^{3.1}$) [see inset on Fig. 4(a)], consistent with a calculation for the specific heat that involves antiferromagnetic spin waves, which gives $C \propto T^3$ (Ref. 19). The departure from the $T^{3.1}$ law below ~ 1.8 K is partly due to the contribution of the ^{141}Pr nuclear Schottky anomaly to the specific heat. For instance, while the measured value of C at $T = 0.55$ K is $C = 128$ mJ/mole K, and the value obtained from the extrapolation of the $T^{3.1}$ line to low temperatures [see inset on Fig. 4(a)] is ~ 9 mJ/mole K, the contribution of the nuclear Schottky anomaly to C can e estimated to be 85 mJ/mole K,[20] thus accounting for most of the discrepancy observed at this temperature. The magnetic entropy in $PrFe_4P_{12}$ reaches R ln2 at ~ 5.5 K and R ln3 at ~ 7 K.

The specific-heat data for $NdFe_4P_{12}$ [Fig. 4(b)] also show a very pronounced peak at $T_M \sim 2$ K that correlates well in temperature with the divergence of χ, the large peak in χ_{ac}, and the sharp drop in ρ. As with $PrFe_4P_{12}$, the behavior of $C(T)$ below T_M for $NdFe_4P_{12}$ [Fig. 4(b)] can be described reasonably well by a T^3 law. However, this is in disagreement with predictions from theoretical calculations involving ferromagnetic spin waves, which yield a $T^{3/2}$ dependence.[19] The magnetic entropy in $NdFe_4P_{12}$ reaches R ln2 at ~ 1.7 K and R ln4 at ~ 7.4 K.

The effect of applied magnetic fields on $\rho(T)$ for $PrFe_4P_{12}$ and $NdFe_4P_{12}$ at low temperatures is illustrated in Figs. 5(a) and 5(b), respectively. The data for $PrFe_4P_{12}$ were taken on a different sample from the one utilized in the measurements of Fig. 1(b). As the temperature is decreased in zero magnetic field, ρ first exhibits a sharp increase at ~ 6.2 K, passes through a maximum at ~ 5 K, a minimum at ~ 3 K, another maximum at ~ 1 K, and then starts to decrease again. The peak in $\rho/\rho_{300\,K}$ versus T at ~ 1 K is rapidly depressed by H and is completely suppressed at $H = 2$ T. The sharp increase in ρ at T_M is depressed by the magnetic field, and is completely suppressed at 6 T. The temperature at which the upper maximum in the $\rho(T,H)$ data of Fig. 5(a) occurs, as well as its magnitude, are depressed by magnetic field, which is consistent with the depression of the magnetic field value necessary to induce the features

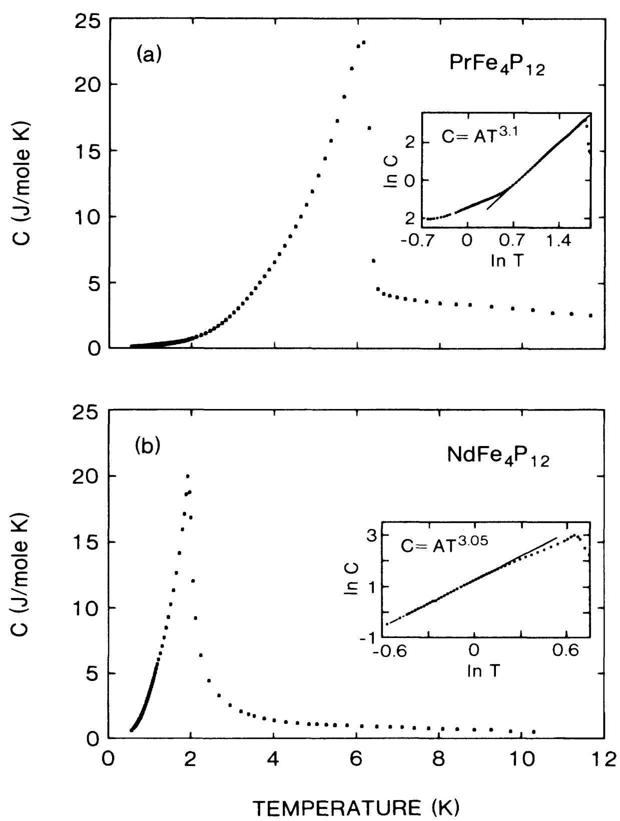

FIG. 4. Specific heat vs temperature for (a) $PrFe_4P_{12}$ and (b) $NdFe_4P_{12}$.

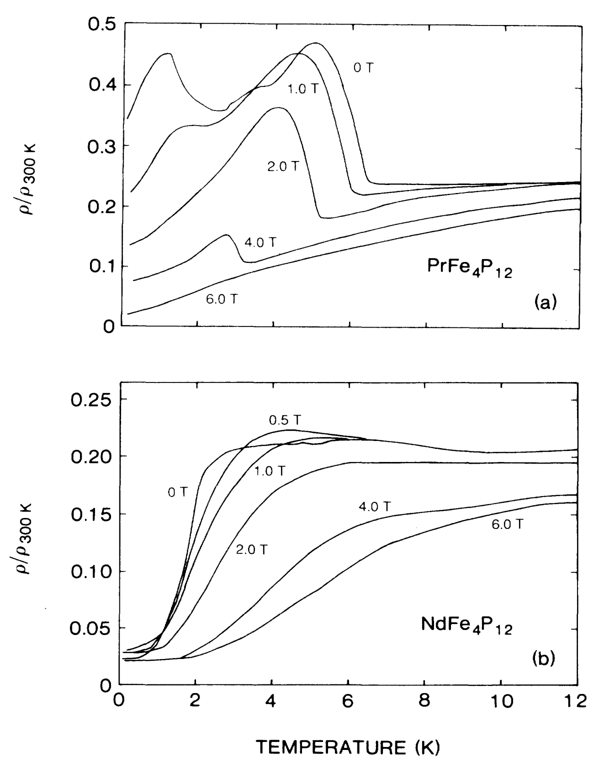

FIG. 5. Behavior of $\rho/\rho_{300\,K}$ vs temperature at various values of applied magnetic field for (a) $PrFe_4P_{12}$ and (b) $NdFe_4P_{12}$.

observed in the magnetization curves below T_M as a function of temperature.

Curves of $\rho/\rho_{300\,K}(T)$ in applied magnetic fields for $NdFe_4P_{12}$ are shown in Fig. 5(b). The sharp drop in $\rho/\rho_{300\,K}$ at $T_M \sim 2$ K is progressively broadened by the applied field. The magnetoresistivity is small and positive in a narrow temperature interval in fields $H < 1$ T, but becomes large and negative at higher fields, which is indicative of magnetic-field-induced ferromagnetic ordering, and consequently, of suppression of spin-flip scattering with onset at $T > T_M$.

CONCLUSIONS

The measurements reported in this paper indicate antiferromagnetism for $PrFe_4P_{12}$ below $T_M = 6.2$ K and ferromagnetism for $NdFe_4P_{12}$ below $T_M = 2.0$ K. The sharp increase in resistivity at T_M for $PrFe_4P_{12}$ is suggestive of Suezaki-Mori–type behavior,[21] in which a peak in $\rho(T)$ can occur near T_M due to partial gapping of the Fermi surface. The sharp reduction of resistivity below T_M for $NdFe_4P_{12}$ is presumably due to a reduction in spin-disorder scattering, while the broad minimum near 33 K is not well understood.

The magnetization measurements on $PrFe_4P_{12}$ below T_M reveal the occurrence of a magnetic-field-induced spin-flop or metamagnetic transition. The magnetoresistance measurements are consistent with this behavior. Magnetization measurements on $NdFe_4P_{12}$ at 1.4 K show a rapid rise to magnetic saturation with very little hysteresis, indicative of weak coercivity. Specific-heat measurements on both compounds show pronounced features at the ordering temperatures, demonstrating that these are bulk magnetic transitions. The specific heat below the ordering temperature displays a nearly T^3 behavior for both of these compounds. Whereas this is consistent with antiferromagnetic magnons in $PrFe_4P_{12}$, it is not consistent with ferromagnetic spin waves expected in $NdFe_4P_{12}$. Similar T^3 behavior of the specific heat was observed below the Curie temperature for the isomorphic compound UFe_4P_{12} (Ref. 15).

The $M Fe_4P_{12}$ series of compounds is particularly rich in its variety of low-temperature magnetic, transport, and thermal properties. Further work to characterize the magnetic behavior of these interesting materials is in order. Measurements of the pressure dependence of the magnetic properties may yield important details of the magnetic interactions and will be reported elsewhere.

ACKNOWLEDGMENTS

The authors would like to thank Mark Kuric for his help in the magnetization measurements on $NdFe_4P_{12}$. This research was supported by the U.S. Department of Energy under Grant No. DE-FG03-86ER45230 at the University of California, San Diego (UCSD), and by the National Science Foundation under Grant No. DMR 82-03690 at Tufts University. One of us (M.B.M.) would like to express his appreciation to the John Simon Guggenheim Foundation for support while part of this work was being carried out.

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