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Magnetic phase transitions in $EuNi_5P_3$: Unusual steps in the magnetization with field

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Magnetization measurements on single crystals of $EuNi_5P_3$ show that it is an antiferromagnet below 0.5 T and 7.5 K. Above 0.5 T and below 7.5 K, there is a series of steps in the magnetization isotherms until saturation is reached. Hysteresis with both field and temperature is observed, as well as a large time dependence of the magnetization at fields near the first step.

Rare-earth intermetallics compounds have attracted much attention in recent years because of their varied and often unusual magnetic properties; the magnetism of many alloys of rare-earth metals and transition metals has been studied extensively.[1] Rare-earth transition-metal silicides, in particular, exhibit a wide range of ground states ranging from heavy-fermion superconductivity and mixed valence to various kinds of magnetic order.[2] Although it is possible to synthesize a large number of rare-earth transition-metal phosphides[3] which are metals and have similar crystal structures to the silicides, the properties of the phosphides have not received as much attention. This is unfortunate because not only are a variety of compositions possible, but these phosphides can be crystallized as near-perfect single crystals from a tin flux. Therefore, rather than settle for measurements on polycrystalline samples, as has been the only choice for many rare-earth intermetallic compounds,[1] it is possible to measure the properties of these phosphides with respect to their various crystallographic axes. We report here the large anomalies and unusual steps in the magnetization versus field of oriented single crystals of $EuNi_5P_3$.

Recently, we reported the synthesis of $EuNi_5P_3$ from a tin flux.[4] This new phosphide crystallizes in the orthorhombic space group *Cmcm* into highly reflective, long, thin needles. The refinement of the crystal structure from single-crystal x-ray data shows that the composition is $EuNi_5P_3$, that there are four formula units per unit cell, and that all the europium atoms are in equivalent positions. The magnetic structure has not been determined. Typical crystals are 12 mm long, a few tenths of a mm on a side, and weigh about 0.3 to 1.6 mg. The x-ray crystallographic data on these crystals show that they are of superior quality. An interesting feature of this compound is that the Eu-Eu distance along the *a* axis, which is the needle axis, is 3.62 Å, while in all other directions the Eu-Eu distance is >6 Å. The subject of this paper is the magnetic behavior of $EuNi_5P_3$ with the magnetic field applied along the europium chains.

Magnetization measurements were made on a SHE model No. 905 superconducting quantum-interference device magnetometer at temperatures from 1.4 to 280 K and at fields to 5 T. Using a Kel-f container, based on the design of Roy, Buchanan, and Ginsburg,[5] the crystals could be oriented accurately with respect to the magnetic field. The container used for these experiments has a small magnetization ($<8\times10^{-4}$ emu at 5 K, 0.5 T); thus the necessary container corrections are about two orders of magnitude smaller than the magnetization values observed for the $EuNi_5P_3$ samples. The needles of $EuNi_5P_3$ (which have the *a* axis parallel to the needle axis) were oriented with the magnetic field along all three crystallographic axes.

The magnetic susceptibility of $EuNi_5P_3$ follows the Curie-Weiss law above 100 K. A fit of the inverse susceptibility versus temperature at 5.0 T for temperatures between 160 and 280 K gives a Weiss temperature of 0.79 K and a moment of $8.02\mu_B$ which is close to the free-ion value of 7.94 for Eu^{2+} ($J=\frac{7}{2}$, $S=\frac{7}{2}$). The saturation magnetization at 5.0 T, 1.5 K is $6.77\mu_B$ again close to the saturation value of 7.0. Thus the europium ions are divalent and are the dominant contribution to the magnetization; it is likely that the contribution from the potentially magnetic nickel ions is small.

The temperature dependence of the magnetization at fields less than 0.5 T oriented along the *a*, *b*, and *c* axes, as shown in Fig. 1, is characteristic of an antiferromagnet with its easy axis parallel to the *a* axis. The Néel temperature is about 7.5 K. The low ordering temperature indicates that the magnetic interactions are weak.

The magnetic behavior changes dramatically as the field is increased. The magnetization isotherm at 4.3 K,

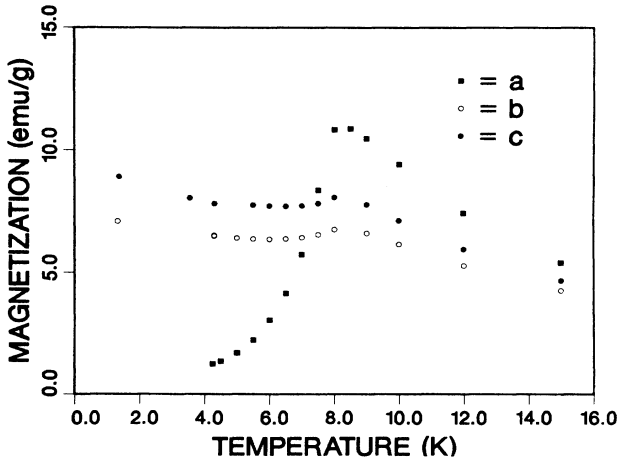

FIG. 1. Magnetization vs temperature for $EuNi_5P_3$ in a field of 0.3 T. Data with the field oriented parallel to the *a*, *b*, and *c* axes are shown.

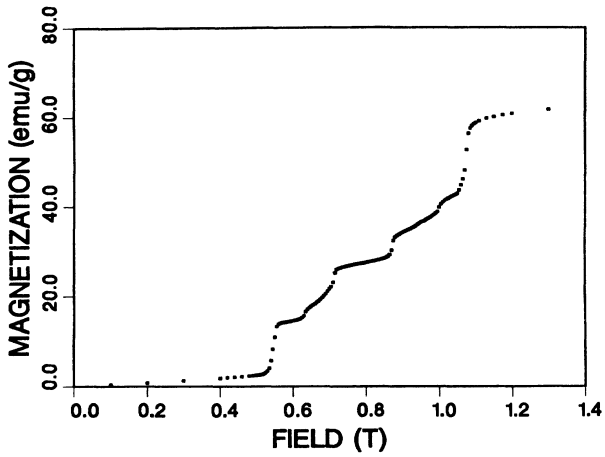

FIG. 2. Magnetization vs field for $EuNi_5P_3$ at 4.3 K with the a axis of the crystal oriented parallel to the magnetic field.

measured with the a axis oriented parallel to the magnetic field, is shown in Fig. 2. Below 0.5 T, the magnetization is linear with field and the magnitude is small as is typical for an antiferromagnet. There is a sharp rise in the magnetization at 0.51 T about which considerable hysteresis in both temperature and field is observed. As the field is increased further, there is a series of small steps of varying magnitude followed by a large final rise in the magnetization to near saturation. There seems to be no obvious pattern to the position of the steps. They are separated by intervals from 0.06 to 0.08 T except for the third and fourth steps which are separated by about 0.17 T. Above 1.05 T the curve is close to flat.

Figure 3 shows two field sweeps at 4.3 K, one from low to high field, the other from high to low field. The hysteresis in the region from 0.5–0.7 T is evident and a small

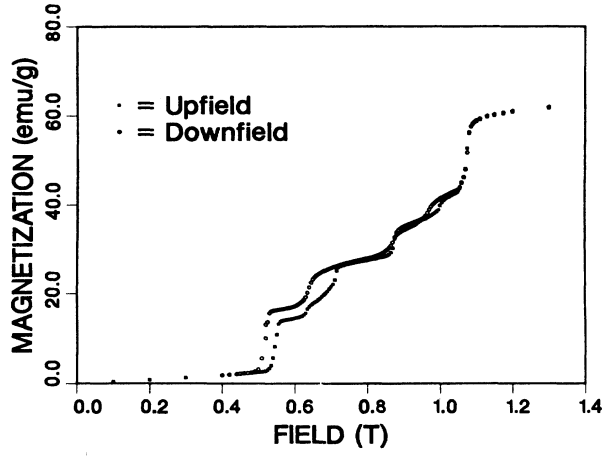

FIG. 3. Magnetization vs field for $EuNi_5P_3$ at 4.3 K with the a axis oriented parallel to the magnetic field. The lower curve was obtained by increasing the field from 0.1 T, while the upper curve was obtained by decreasing the field from 5 T. The hysteresis near the transition at 0.50–0.55 T and at subsequent steps is evident.

amount of hysteresis is observed also around the subsequent steps. Since there is hysteresis around the steps, we conclude that these transitions are first order. The initial rise in magnetization near 0.50–0.55 T is due most likely to a spin flop. The low anisotropy observed, as evidenced by the small spin-flop field, is characteristic of intermetallic compounds containing divalent europium, an S-state ion in which the crystal-field splitting and single-ion anisotropy are low.[6] Since the europium ions are located in chains along the easy a axis, we assume that the exchange anisotropy makes a large contribution to the observed anisotropy.

There is a time dependence associated with the first rise in the magnetization near 0.50–0.55 T. It takes several hours for the magnetization values to become constant at field values near this first step. The rate of change of the magnetization decreases slowly with time and the magnetization can be fit to $M = M_0 + S\ln(1 + t/t_0)$, where, typically, $S = 0.56$ emu/g, $M_0 = 9.3$ emu/g, and $t_0 = 6.69$ min. This type of time dependence usually is associated with the motion of thermally activated domain walls.[7] The movement of the domain walls also can be retarded by the presence of lattice defects or impurities. The presence of tin impurities might be important and should be checked carefully. Previous analyses on similar materials (for example, $EuNi_2P_2$) have shown this tin impurity to be less than 0.2 wt.%.

Figure 4 shows field sweeps at 4.3, 5.5, and 8.0 K. At 5.5 K, the steps in the magnetization are less sharp and have moved downfield compared with those at 4.3 K; only a small remnant of the structure observed at lower temperature remains. The curve at 8 K, above the Néel temperature, is completely smooth. As the temperature is increased, larger magnetic fields are needed to reach the saturation magnetization.

The magnetization curves obtained when the crystals are oriented with the applied field along the b and c axes are smooth with field, with initial linear behavior, and subsequent saturation is at about 3.0 T. As shown in Fig. 5, both transverse magnetizations (b and c axes) are

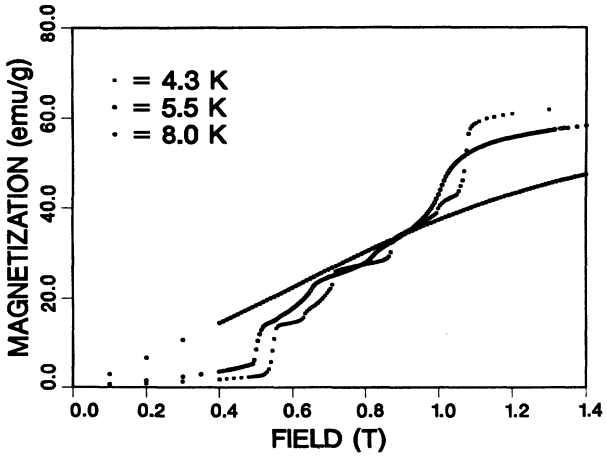

FIG. 4. Magnetization vs field for $EuNi_5P_3$ for the crystals oriented with the magnetic field applied parallel to the a axis. Isotherms at 4.3, 5.5, and 8.0 K are shown.

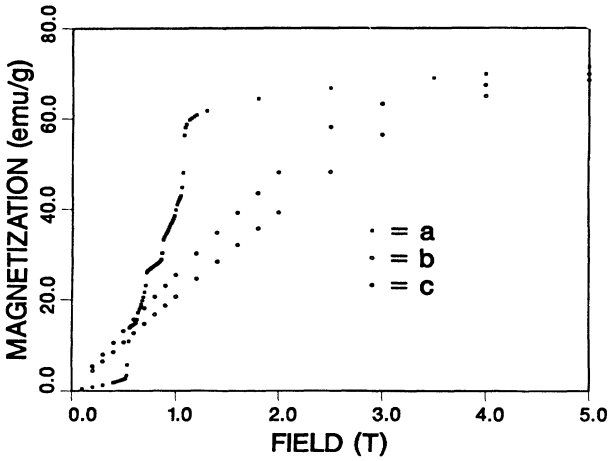

FIG. 5. Magnetization vs field for $EuNi_5P_3$ at 4.5 K for the crystals oriented along all three axes. Corrections for demagnetizing effects have not been applied.

higher than the longitudinal one (*a* axis) for fields below 0.5 T. In the 0.5–0.6-T range, magnetizations for the *a* and *c* axes are similar. Above 0.6 T and up to saturation values, the transverse curves are below the *a*-axis curve.

Since $EuNi_5P_3$ has a high volume susceptibility, it is important to consider corrections for the internal field. No demagnetizing corrections were performed for the measurements with the needle axis oriented parallel to the field; it was assumed that, since the needles were long and thin, this correction was unnecessary. However, when the $EuNi_5P_3$ crystals were oriented perpendicular to the applied field, the demagnetizing corrections are quite significant. At 5.0 T, the correction is estimated to be about 0.4 T. The data presented in the figures in this paper have not been corrected for demagnetizing effects. We note that if the perpendicular magnetization is corrected for demagnetizing effects, the new values for the magnetization near 5.0 T become closer to those obtained for the parallel orientation.

Before discussing the origins of the unusual magnetic behavior, it is useful to discuss the transport properties of these crystals. Resistivity measurements were made along the *a* axis using a four-probe technique at temperatures from 13 to 300 K. A 37-Hz alternating-current source and lock-in detection were used. The resistivity along the needle axis decreases slowly with decreasing temperature from 50 to 10 $\mu\Omega$-cm. Because of the uncertainties in the sample geometry, the absolute values of the resistivities are approximate. However, based on the magnitude and temperature dependence, we conclude that $EuNi_5P_3$ is a metal.

Because of its metallic character, the most likely mechanism for the exchange interactions between europium ions is through Ruderman-Kittel-Kasuya-Yosida-(RKKY) type interactions.[8] However, since the moment is so large and the ordering temperature so low, a contribution from dipolar interactions cannot be ruled out. There are several possible origins to the steps in the magnetization. In particular, a series of spin-flop transitions of the various magnetic sublattices is likely. The anisotropic character of the crystal [quasi-one-dimensional (Q1D)] and the metallic behavior do not completely rule out, on the other hand, a possible modification of the magnetism because of Fermi-surface effects.[9] Since the Eu^{2+} exchange interactions could be of the RKKY type, the quantization of electron orbits in a magnetic field may give rise to the unusual magnetization isotherms observed. The high magnetic fields, low temperatures, and superior crystal quality make the observation of quantized phenomena a possibility. Lower-temperature magnetization versus field sweeps might reveal more steps and the complex field dependence usually observed in Q1D metals.[9] It should be noted, however, that all reported experiments for Q1D systems exhibit a strong transverse and weak or nonexisting longitudinal behavior, whereas the reverse is true for $EuNi_5P_3$.

There are few rare-earth compounds which have been reported to show behavior similar to $EuNi_5P_3$. Both $NdCu_6$ and CeSb have complex magnetization isotherms with a series of steps.[10,11] However, in both of these materials the magnetic anisotropy is larger and the transitions occur at considerably higher fields. The magnetic data for CeSb have been interpreted in terms of the axial next-nearest-neighbor Ising (ANNNI) model.[12] Similar steplike behavior has been observed in $EuAs_3$, a compound with a monoclinic structure in which the Eu atoms, like those in $EuNi_5P_3$, lie in chains. This material exhibits a modulated magnetic structure which is commensurate or incommensurate with the lattice depending on temperature and field.[13] In order to understand the origins of the magnetic behavior observed for $EuNi_5P_3$, it is important to have neutron diffraction, heat capacity, lower-temperature magnetization, and magnetoresistance data.

In summary, the magnetization isotherms for $EuNi_5P_3$ with the field parallel to the *a* axis show an unusual series of steps. The sharp transition near 0.5 T is first order and may be caused by a spin flop. The possibility that the intriguing behavior is observed is a Fermi-surface effect, caused by the quantization of electron orbits in a magnetic field and their interactions with the europium moments, warrants further investigation.

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