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Metamagnetism and giant magnetoresistance of the rare-earth intermetallic compounds R_2Ni_2Pb (R=Er,Ho,Dy)

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We have measured the magnetization and magnetoresistance for a series of rare-earth (R=Er,Ho,Dy) plumbide intermetallic compounds, R_2Ni_2Pb. These materials form in an unusual orthorhombic structure with space group $Cmmm$. After multiple magnetic transitions, the ground state exhibits a steplike series of large-moment metamagnetic transitions in low fields (1–2 T) concomitant with switchinglike properties of the magnetoresistance where sharp changes of up to 30% are found. We relate these properties to the layered magnetic structure of the compound.

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Technological progress is often made with new materials possessing innovative properties. Of particular importance are the magnetic materials that exhibit large changes in their electronic properties as a function of an applied magnetic field. In recent years, enormous interest has been devoted to the artificial multilayer structures displaying giant magnetoresistance (GMR) [Refs. 1,2] and to magnetic oxides that show a metal-insulator transition, called a colossal magnetoresistance.[3,4] There also exists a further class of materials where large magnetoresistance effects are possible, namely, rare-earth (R) and actinide (U) intermetallic compounds,[5–8] and ongoing material efforts are underway to find and stabilize new compounds.[9]

A new magnetic system was discovered, R_2Ni_2Pb (R =Gd to Lu), possessing an unusual crystal structure (space group $Cmmm$).[10] These plumbide compounds can be synthesized in single-crystal form with the heavy rare earths (Gd to Lu) where large magnetic moments and strong crystal-field anisotropies are present. Hence, we would expect unconventional magnetic ordering and strong magnetic-field dependences. Indeed, these materials exhibit multiple magnetic transitions[11,12] whose magnetic structure is complicated (multiple $\vec{Q}$ vectors) and is yet to be determined by neutron scattering.[13] Here, we present the low-temperature ground-state behavior of the magnetization and magnetoresistance for three such compounds: Er_2Ni_2Pb, Ho_2Ni_2Pb, and Dy_2Ni_2Pb in single-crystal form. These systems exhibit a steplike series of large-moment metamagnetic transitions in rather low fields (1–2 T) concomitant with switchinglike properties of the magnetoresistance where sharp changes of up to 30% are found along certain crystallographical directions. In other directions, a monotonically increasing magnetoresistance persists up to very large fields (25 T). We relate these effects to the layered magnetic structure that can be field switched to a fully ferromagnetic ground state. Such changes in the magnetism cause superzone reconstructions in the Fermi surface that increase the conductivity.

The crystal structure of R_2Ni_2Pb, shown in Fig. 1, adopts the AlB_2Fe_2-type configuration ($Cmmm$). The salient features of this structure are the packing sequence of Ni-centered trigonal [NiR_6] prisms, Pb-centered slightly distorted cubes [PbR_8], and the R-centered distorted pentagonal [RNi_6Pb_4] prisms. An alternative way to describe the structure is as a naturally occurring multilayer with a-c planes of R and Pb atoms intercalated between a wavy plane of Ni atoms in the sequence: Pb-R-Ni-R-Pb-R-Ni-R-Pb along the b axis (see Fig. 1). Note that in this structure all the R atoms in the unit cell are crystallographically equivalent and possess a highly asymmetric nearest-neighbor environment. The room-temperature powder x-ray-diffraction (XRD) measurements determined that the sample has an orthorhombic structure with a=4.02 Å, b=13.94 Å, and c=3.63 Å for Ho_2Ni_2Pb (similar values for the unit-cell constants were found for Dy and Er compounds). The single-crystal determination and quality was made with Laue XRD.

In order to synthesize these materials, the constituent elements were arc-melted in the desired ratio on a water-cooled copper hearth under high-purity argon gas. Special care was taken to ensure that the lead did not evaporate upon

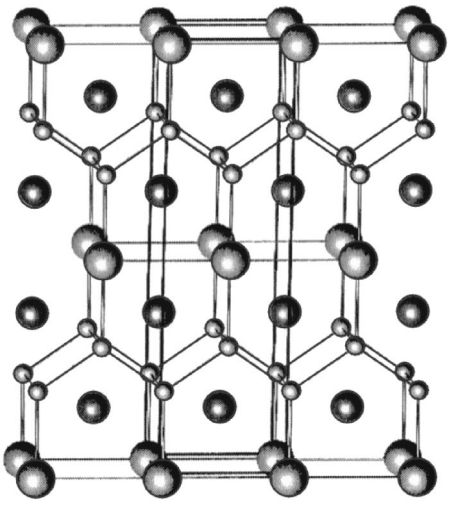

FIG. 1. Orthorhombic crystal structure ($Cmmm$) of R_2Ni_2Pb. The unit cell is indicated by the dark lines. The largest, medium, and smallest size of atom representation are Pb, R, and Ni, respectively.

TABLE I. Basic magnetic properties of the *R*-221 compounds. Θ_{CW} is the paramagnetic Curie-Weiss temperature, T_N represents the Néel temperature (no net moment formed), T_C the Curie temperature where there is a net moment, and μ_{eff} and μ_{sat} are the Curie-Weiss and field saturation moments.

Compound	Θ_{CW}	T_N(K)	T_C(K)	μ_{eff} (μ_B)	μ_{sat} (μ_B)
DY_2Ni_2Pb	+10	14.5	3.5	10.5	8.5
Ho_2Ni_2Pb	+10	6.8	4.8	10.6	8.0
Er_2Ni_2Pb	+15	3.4, 3.2, 2.0		9.5	9.0

initial melting. To guarantee homogeneity, the alloy buttons were remelted several times. Through a controlled slow removal and temperature reduction of the arc, high-quality single-crystal platelets, a few mm^2 in area, were found to grow naturally out of the melt. This ''self-growth'' process was optimized via tuning the cooling protocol to produce the largest crystals in the a,b, and c orientations. All samples were analyzed using electron probe microanalysis (EPMA) that proved them to be single phase (second phases are less than 5 vol %) and to have the desired 2:2:1 stoichiometry (within 2% resolution).

We performed magnetization $[M(H)]$ measurements at 1.8 K on a quantum design superconducting quantum interference device (SQUID) magnetic property measurement system. The magnetoresistance $\rho(H)$ was measured at 1.8 K using a quantum design physical property measurement system. A collection of the magnetic ordering temperatures and effective moments are shown in Table I for the three compounds under study.

We now focus upon the low-temperature magnetic behavior of single crystal Dy_2Ni_2Pb, Ho_2Ni_2Pb, and Er_2Ni_2Pb, especially on the field dependence of their magnetization and magnetoresistance. Figure 2 shows a compilation of our magnetization result in μ_B per *R* atom. For Dy_2Ni_2Pb [Fig. 2(a)] the easy axis is *c* and after a two step-hysteretic transition, full saturation ($8.4\mu_B$) is obtained around 2 T. The *a* axis follows a similar behavior, except that the switching fields are shifted to somewhat higher values and full saturation is not yet reached at 3 T. Strikingly different is the *b* axis (hard) where there is only a slow and steady (reversible) increase and decrease in the magnetization up to 6 T and back. For Ho_2Ni_2Pb [Fig. 2(b)] a three-step metamagnetic transition now occurs along the *a* axis saturating at 1 T, while the *c* and *b* axes are featureless and slowly rising. Finally, for Er_2Ni_2Pb [Fig. 2(c)] a subtle, smeared-out two-step transition is indicated for the *b* (now easy) and *c* axes, but the *a* axis appears to only show a small and monotonically increasing magnetization as a function of the field. Upon expanding the scale of the *a*-axis magnetization, delicate steps can be gleaned in $M_a(H)$ between 1 and 2 T. Here (see Table I) the lowest transition temperature (2.0 K) is very close to the measurement temperature (1.8 K), which could remove the sharpness of the transitions. Comparatively, there is clearly a variety of metamagnetic transitions among the three rare-earth magnetic elements as the easy axis changes from *c* to *a* to *b*, and the transitions are either two or three step, unusually sharp with some regions of hysteresis. Note that all the switching behavior occurs around or below 2 T.

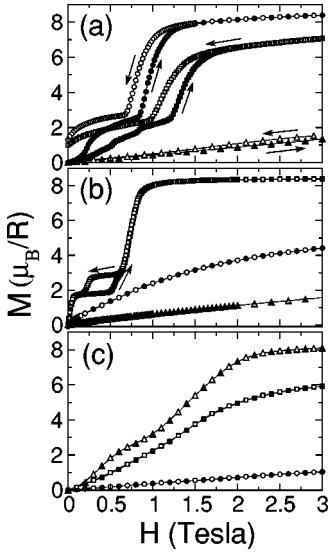

FIG. 2. Magnetization (M) vs field (H) at 1.8 K for (a) Dy_2Ni_2Pb, (b) Ho_2Ni_2Pb, and (c) Er_2Ni_2Pb. Close (open) symbols stand for increasing (decreasing) the field. Square, triangle, and circle are for a,b and c axes, respectively. The arrows in (a) and (b) indicate hysteretics of the magnetizations.

Let us now examine the effect of the metamagnetic transitions on the magnetoresistance properties. Figure 3 compiles the results as $\Delta\rho/\rho_0 \equiv [\rho(\mathrm{H}) - \rho(0)]/\rho(0)$ in percent and uses fields up to 10 T (only the range from -3 T to 3 T is shown in Fig. 3). Now we notice giant changes in the magnetoresistance ($\approx 25\%$) at the transition field.[14] For Dy [Fig. 3(a)] there are sharp decreases at 1 T (c axis) and 2 T (a axis) while the b-axis $\Delta\rho$ oscillates slightly positive and slightly negative, and then continues with a linear, positive

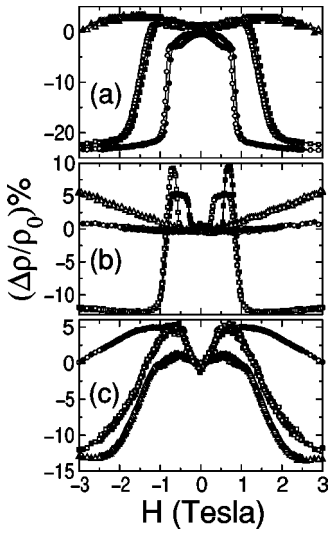

FIG. 3. Normalized (percent) change in magnetoresistance vs field H at 1.8 K for (a) Dy_2Ni_2Pb, (b) Ho_2Ni_2Pb, and (c) Er_2Ni_2Pb. As in Fig. 2, close (open) symbols stand for increasing (decreasing) the field. Square, triangle, and circle are for a,b and c axes, respectively.

slope to our largest field. For Ho [Fig. 3(b)], both the *b* and *c* axes exhibit the latter linear behavior with 20% and 5% increase, respectively. The *a* axis first shows a positive magnetoresistance but then switches (stepwise) at 1 T to a negative value with a net change of $\approx 25\%$. Finally, for Er [Fig. 3(c)] all three directions display an initially positive $\Delta\rho$ followed by clear decrease in the magnetoresistance with rather sharp *b* and *c* axes. Above 2 T the *b* axis, as for the Dy and Ho, resumes its positive slope and should have a positive $\Delta\rho/\rho_0$ value around 10 T (not shown in the figure). We have very recently extended the magnetic-field range for $\Delta\rho$(H) using the high-pulsed field facility at Los Alamos National Laboratory (LANL). For Ho_2Ni_2Pb with the field oriented along the hard axis (*b* axis), we observed a weak positive H^2 dependence at the lowest fields (≈ 0.5 T). This is followed by a strong positive linear field dependence that shows indications of saturation around 20 T. In this case an increase in $\Delta\rho \approx 30\%$ was detected. At a field of 23 T, the Ho sample suddenly exploded due to the enormous magnetostrictive forces present. Similar explosive behavior was found for Dy-221[*b* (hard)axis] which was also lost during a 50-T pulse.

Based upon the unusual crystal structure and a favorable combination of magnetic properties, the 221 intermetallic compounds exhibit a series of multiple-step metamagnetic transitions. Here, between the steps there is a large increase in the net magnetic moment up to $6\mu_B$, according to the direction of the field with respect to the crystallographic axes. These transitions occur in rather low fields, $H<2$ T and are very sharp depending on the particular easy axis of the given *R* element. A criterion for such transitions is that the measurement temperature should be below the lowest magnetic critical temperature (see Table I) e.g., $T<3.5$ K for Dy-221. By substituting different transition-metal (*T*) elements, e.g., Mn or Fe, for Ni or using other *R* elements (Gd or Tb), we expect to significantly increase this temperature. Due to strong crystalline anisotropy in combination with the crystalline electric field of the *R* atom, the ground-state magnetic structure is not a simple ferromagnet, and most probably forms an uncompensated antiferromagnetic (ferrimagnet) or a canted spin alignment. Neutron-diffraction and magnetic structure determinations are in progress to establish the exact ground state.[13] By applying an external field along a particular crystal axis, we can ferromagnetically orient the entire spin system along the field. The sharp jumps along certain axes are a cooperative effect and not a temperature activation $[\exp(E_b/k_BT)]$ of clustered spins over an anisotropy energy barrier (E_b). This indicates that the magnetic exchange interaction, which is also anisotropic, strongly couples together the complete spin system. Thus, we have a magnetic-field induced phase transition whose hysteresis suggests that it is of first order.[15]

Associated with the metamagnetism is a peculiar GMR clearly related to switching of the magnetic moments. To the best of our knowledge, a similar behavior has been observed in only three rare-earth intermetallic compounds very recently.[6–8] Two of them, however, do not show saturation in applied fields above 5 T in any crystallographic axis and their multiple stepwise metamagnetic transitions are rather small.[6,8] The magnetoresistance of $CeTe_2$ compound does not show a sharp jump for the critical magnetic fields in any axes direction.[7] The GMR of R_2Ni_2Pb exhibits an abrupt and negative change in the resistivity at a critical field close to that of the metamagnetic transition. Drops of up to 25% in $\Delta\rho/\rho_0$ are observed at fields around 1 T. There are also precursor effects where a small (10%) and positive magnetoresistance first appears before the large negative one. The associated hysteresis behavior in $\Delta\rho$ is rather small, $\Delta H \equiv 0.1$ T. After the negative step, $\Delta\rho$ for the *a* and *c* axes remains relatively constant, i.e., saturated for all three compounds. However, for the *b* axis there is a linear in field upturn that causes the magnetoresistance to become positive. Over our 9-T range of field, an increase of $\Delta\rho$ up to 20% is possible without any indications of saturation. An interesting new effect is produced by mechanically rotating the sample (or field direction) in constant field between easy and hard axes, thus changing the MR from negative to positive. Total variations of 30–35 % in the magnitude of the resistance are obtained by these mechanical oscillations. Once again the GMR may be tuned and maximized for nonpreferential axis orientations or for the proper choice of *T* and *R* elements.

The physics of GMR is clearly related to the strong spin scattering of the *R* local moments in a layered structure. A perfect (or complete ferromagnetic) alignment of these moments with the field causes a large decrease in the resistivity. And since the field alignment is rather sudden the resistivity drops sharply. Such an effect is similar to the ferromagnetic spin alignment of the multilayers in the thin-film GMR causing the drop.[1,2] For our 221 compounds, the magnetic rare-earth atoms are positioned in the *a*-*b* plane perpendicular to the *c* axis (see Fig. 1). We assume that these atoms are most strongly coupled magnetically in the plane while a weaker coupling exists along the *c* axis. With the application of an external field, we switch on to a complete three-dimensional ferromagnetic alignment of the moments, thus the analogy with the thin-film multilayers.

Theory applied to the uranium compounds has drawn much the same comparison and shown that the field dependence of the conductivity (linear-response approach) is correlated with the band structure and corresponding Fermi surface (FS).[16,17] Up on metamagnetic transitions the antiferromagnetic state transforms to the ferromagnetic one, and a large superzone reconstruction of the FS occurs. These calculations show the conductivity to greatly increase with the field ($\approx 50\%$) depending upon the particular change of FS sheet or topology.[16,17] The small positive precursor in $\Delta\rho$ is due to fluctuations (or instabilities) in the FS, incipient to its restructuring. Now the $M(H)$ is essentially constant and the conductivity decreases by only $\approx 5\%$. However, there also exists in the R-221 compounds a hard axis (depending on the crystal fields of the specific *R* atom) where the spins cannot be aligned even in 10 T. Here the MR has a positive slope that continues to increase. This means that another different mechanism for the MR comes into play such that the net scattering become greater. We consider this to be a nonspin dependent scattering (it occurs in nonmagnetic Y_2Ni_2Pb) whereby the number of charge carriers continuously decreases due to field induced changes in the FS and density of states along certain directions in κ space. Cer-

tainly the large positive MR cannot be caused by a simple orbital or Lorentz force scattering of the charge carriers. Hall-effect measurements would detect such variations in the number of carriers or their density of states. To interpret both the negative and positive MR effects, band-structure calculations[18] are underway to determine the spin disorder and Fermi-surface scattering in these anisotropic 221 magnetic compounds.

In conclusion, we have observed sharp, first-order metamagnetic transitions in the magnetization, concomitant with large changes in the magnetoresistance for a series of R-221 plumbide compounds. Depending upon the particular rare earth (Dy, Ho, Er), the transitions occur along different crystallographic axes. Using the layered structure analogy, we expect significant modifications (or increases) in the Fermi surface to be caused by the field-induced antiferromagnetic to ferromagnetic transitions, and thereby enhancing the conductivity.

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