Large Negative Magnetoresistance of the Rare-Earth Transition-Metal Intermetallic Compound $PrMnSi_2$

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The rare-earth intermetallic compound $PrMnSi_2$ consists of two magnetic sublattices, i.e., layers of Mn atoms and layers of Pr atoms, which repeat in the $(-Mn-Pr-Pr-)_\infty$ sequence. Electrical resistivity measurements were carried out for $PrMnSi_2$ between 2 and 350 K under various magnetic fields. $PrMnSi_2$ is a metal with two metal-to-metal transitions at ~20 and ~50 K, and its resistivity vs temperature curves show a significant hysteresis in the absence and presence of an external magnetic field. The resistivity is reduced by an external magnetic field, and this negative magnetoresistance reaches up to 47% at 9 T around 17 K where $PrMnSi_2$ is antiferromagnetic at zero field. The magnetoresistance vs temperature curves of $PrMnSi_2$ reveal three peaks at fields up to ~3 T, which correspond to the three magnetic phase transitions of $PrMnSi_2$ observed from magnetic susceptibility and heat capacity measurements. The negative magnetoresistance and the resistivity hysteresis of $PrMnSi_2$ were accounted for by considering how the scattering of the electrons at the Fermi level is reduced by an applied field.

1. Introduction

Due largely to their potential applications in magnetic storage devices, the phenomenon of magnetoresistance in various materials has received much attention in recent years. Artificially multilayered magnetic thin films exhibit a negative giant magnetoresistance (GMR),[1] i.e., a strong decrease in electrical resistivity under external magnetic field. In general, this phenomenon originates from electron scattering by spin sites, which is reduced when the spin moments of these sites become oriented along the direction of an applied magnetic field.[2] GMR has also been observed for several bulk materials such as $SmMn_2Ge_2$,[3] UNiGa,[4] FeRh,[5] $LnGa_2$,[6] and $LnCo_2$ (Ln = rare-earth metal).[7] $SmMn_2Ge_2$ and UNiGa are similar to artificially multilayered GMR materials in that they contain layers of magnetic elements, and such "naturally multilayered" materials might exhibit interesting magnetic properties.[3] The term colossal magnetoresistance (CMR) was initially coined for magnetoresistance with field-induced resistance drop of several orders of magnitude and is now used to describe a large negative magnetoresistance of a bulk material associated with a ferromagnetic ordering near its ferromagnetic transition temperature.[8,9] CMR was first found for mixed-valence compounds $Ln_{1-x}A_xMnO_3$ (Ln = rare-earth metal, A = Ca, Sr, Ba, Pb)[10] and then for non-mixed-valence compounds $Tl_2Mn_2O_7$,[11] $Fe_{1-x}Cu_xCr_2S_4$,[8] $Eu_{14-x}A_xMnSb_{11}$ (A = Ca, Sr),[9] and GdI_2.[12]

The rare-earth transition-metal intermetallic compound $PrMnSi_2$ is a naturally multilayered magnetic compound. As depicted in Figure 1, its structure contains square-net layers of Mn atoms, which repeat along the *b*-direction with the interlayer distance of 8.8 Å.[13] The Mn layers are linked

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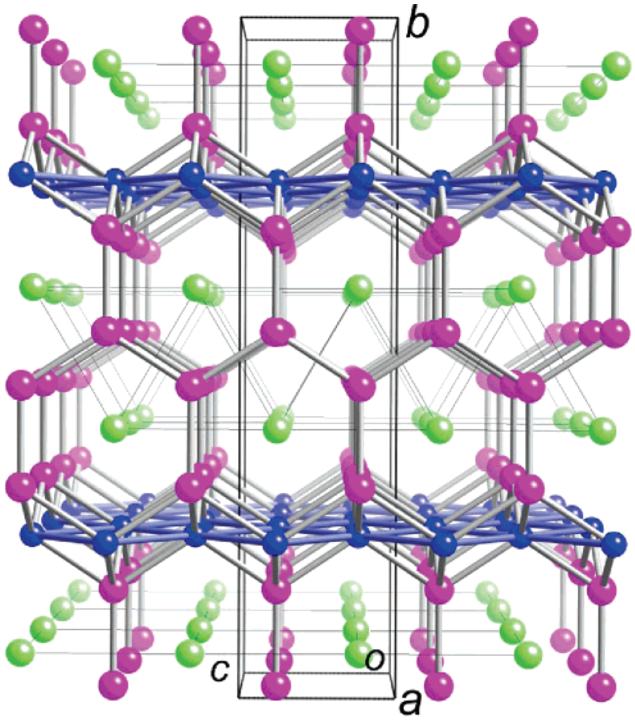

Figure 1. Perspective view of the crystal structure of $PrMnSi_2$. The vertical axis is the *b*-axis. The green, blue, and pink spheres refer to Pr, Mn, and Si atoms, respectively.

together by the Si-ribbon chains running along the *c*-direction, and Pr atoms reside between the Si-ribbon chains. Thus, $PrMnSi_2$ contains two distinct magnetic subunits, i.e., layers of Mn atoms and layers of Pr atoms, which repeat in the $(-Mn-Pr-Pr-)_\infty$ sequence along the *b*-direction. The Mn layers of $PrMnSi_2$ are further separated than those of the naturally layered GMR compound $SmMn_2Ge_2$ by a factor of 1.6. $PrMnSi_2$ was reported[13] to be ferromagnetic up to 434 K, but antiferromagnetic below 35 K. According to a neutron diffraction study,[14] the ferromagnetic ordering occurs only among the Mn atoms and the magnetic moment of Mn at room temperature is approximately 2 μ_B parallel to the *b*-axis. The magnetic structure at 4.2 K shows that the Mn moments within each Mn layer are ferromagnetically coupled, so are the Pr moments within each Pr layer, and adjacent magnetic layers (i.e., between the Mn and Pr layers and between the Pr layers) are antiferromagnetically coupled. The estimated magnetic moments of Mn and Pr below 35 K are respectively 2.35 and 2.04 μ_B aligned parallel to the *b*-direction.[14] In the temperature region where $PrMnSi_2$ is antiferromagnetic at zero field, the magnetic structure of $PrMnSi_2$ is converted to ferromagnetic by applying a magnetic field higher than 5 T.[13] Recently, we have shown[15] that $PrMnSi_2$ exhibits thermal hysteresis in the magnetic susceptibility and magnetic hysteresis in the magnetization. The magnetic susceptibility and heat capacity measurements indicated[15] that $PrMnSi_2$ undergoes three magnetic phase transitions, two below ~20 K and one at ~50 K. The two low-temperature phase transitions do not change the overall antiferromagnetic state. In the present work we examined

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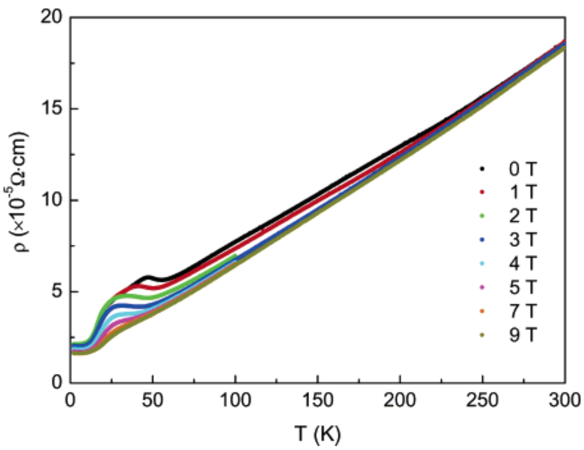

Figure 2. Temperature dependence of the electrical resistivity ρ of $PrMnSi_2$ measured at various magnetic fields.

how the electrical resistivity of $PrMnSi_2$ is affected by external magnetic field. In the following we report results of these magnetoresistance measurements and discuss their implications on the magnetic structure of $PrMnSi_2$.

2. Experimental Section

Samples of $PrMnSi_2$ were prepared by arc-melting appropriate amounts of the elements and subsequent annealing of the melts in Ta tubes. Synthesis and characterization of stoichiometric samples were described in detail in our previous study.[15] For magnetoresistance measurements, a bar of dimension 1 mm × 1 mm × 12 mm was cut out from a piece of $PrMnSi_2$ and mounted in the variable temperature insert of an Oxford ^4He cryostat with the magnetic field perpendicular to its long axis. The resistance was measured using the four-probe technique with a HP 34420A nanovoltmeter.

3. Results and Discussion

3.1. Metal-to-Metal Transition. The resistivity vs temperature (ρ vs T) plots determined at various applied magnetic fields up to 9 T are presented in Figure 2. The measurements were carried out while gradually warming the sample that was first cooled to 2 K at zero field. The values of the resistivity are in the range of 20−200 $\mu\Omega$cm, and the observed metallic character is consistent with our electronic band structure calculations.[15]

The zero-field ρ vs T plot shows a metallic behavior with two weak metal-to-metal transitions at ~20 and ~50 K. The resistivity in the region of ~20 to ~50 K is slightly higher than expected from the slope of the ρ vs T curve above ~50 K, with the same slope as that of the ρ vs T curve above ~50 K. The two transition temperatures correspond well to the magnetic phase transitions observed from our magnetic susceptibility and heat capacity measurements.[15] This indicates that the magnetic interactions are responsible for the resistivity anomalies. The resistivity decrease on raising the temperature through ~50 K corresponds to the antiferromagnetic-to-ferromagnetic transition and hence should be related to a reduced electron scattering by spin sites in the temperature region where the Mn sublattice is ferromagnetic.[14] Likewise, the resistivity decrease on lowering the temperature through ~20 K suggests that the two magnetic

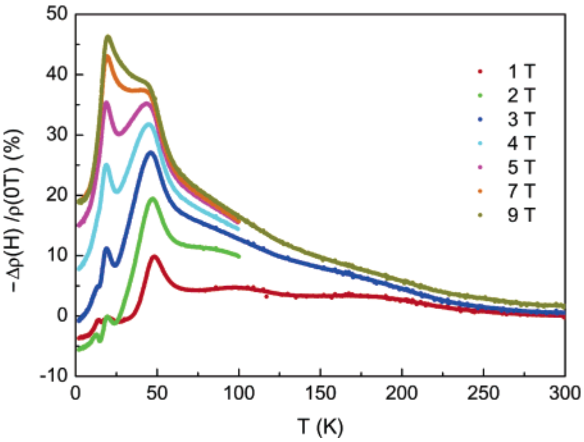

Figure 3. Temperature dependence of the magnetoresistivity $\Delta\rho(H)/\rho(0)$ of $PrMnSi_2$ derived from Figure 2.

phase transitions taking place below ∼20 K lead to antiferromagnetic states with more ordered spin moments, thereby reducing the extent of electron scattering.

3.2. Magnetoresistance. Figure 2 shows that, at any given temperature, the resistivity decreases with increasing the external magnetic field, and the extent of this decrease is greater at a lower temperature. The magnitude of the resistivity anomaly in the ∼20 to ∼50 K region decreases with increasing the external magnetic field, with a faster decrease in the region of ∼50 K than in the region of ∼20 K, and the anomaly is eventually suppressed at 9 T. To explain this magnetoresistance phenomenon, a number of important experimental observations should be recalled: (a) Above ∼50 K, the spins of the Mn layers are ordered ferromagnetically within each layer and between adjacent layers, while those of the Pr lattice are disordered.[14] (b) Below ∼50 K, the spins of the Pr sublattice begin to order, and those of adjacent Mn layers begin to order antiferromagnetically while maintaining a ferromagnetic order within each layer. (c) Below ∼50 K, a strong external magnetic field can induce an antiferromagnetic-to-ferromagnetic transition in the Mn sublattice. (d) The magnetization of $PrMnSi_2$ at high fields (e.g., above 5 T at 45 K) increases linearly with increasing the field,[15] which indicates that the Pr sublattice follows paramagnetic behavior, and hence the spins of the Pr sublattice are largely disordered even under high magnetic field. According to the observations (a)−(d), the magnetoresistance above ∼50 K should be related to a field-induced spin alignment in the Pr sublattice and that below ∼50 K to both a field-induced spin alignment in the Pr sublattice and a field-induced antiferromagnetic-to-ferromagnetic transition in the Mn sublattice.

To examine the field-induced change in the electrical resistivity in more detail, we present in Figure 3 the magnetoresistance vs temperature plots, $-\Delta\rho(H)/\rho(0)$ vs T, where $\Delta\rho(H) = \rho(H) - \rho(0)$, and $\rho(H)$ is the resistivity at an external magnetic field H. These curves exhibit three distinctive peaks when $H <$ ∼3 T. The peak positions are close to the three magnetic phase transition temperatures reported previously.[15] A maximum of 47% suppression of the resistivity is found at ∼17 K at $H = 9$ T. However, a significant negative magnetoresistance persists even at temperatures above ∼50 K, where the spins of the Mn sublattice

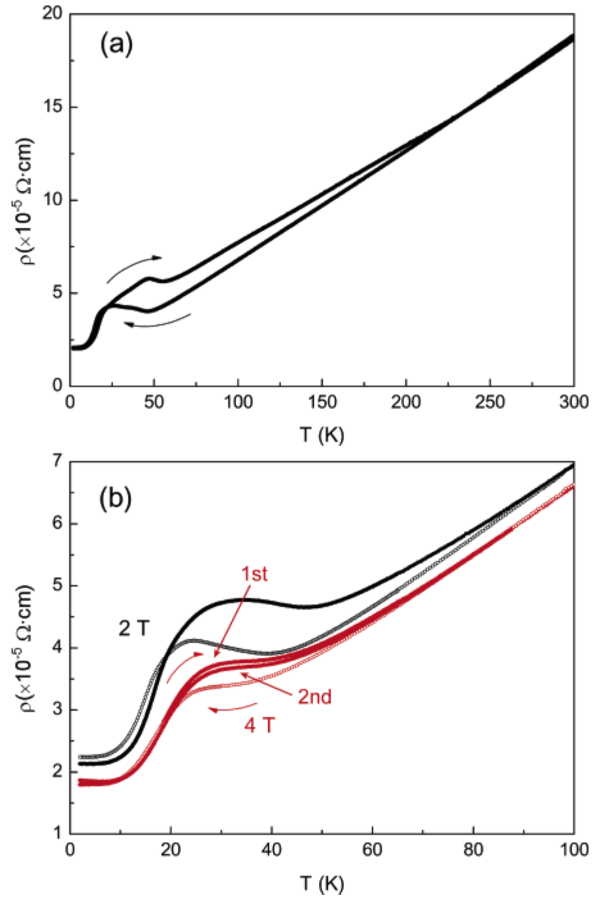

Figure 4. Temperature dependence of the electrical resistivity ρ of $PrMnSi_2$ measured for the cooling and warming cycles at various magnetic fields. (a) At zero field using the sample first cooled. (b) At 2 T (black) and 4 T (red) using the sample first cooled. The solid and open dots represent the heating and cooling cycles, respectively. The warming cycles were obtained twice at 4 T; the first warming cycle with zero-field cooled sample and the second warming cycle with at first zero-field cooled and the second cooled at 4 T.

are ferromagnetically ordered but the spins of the Pr sublattice remain disordered. This magnetoresistance above ∼50 K diminishes slowly with increasing temperature.

A large negative magnetoresistance in a temperature region supporting ferromagnetism requires strong electron scattering by spin fluctuation.[16,17] In the ferromagnetic region of $PrMnSi_2$ (i.e., above ∼50 K), the spins of the Mn sublattice are ferromagnetically ordered, but the spins of the Pr sublattice are disordered. Upon applying a magnetic field, the Pr magnetic moments become gradually aligned, so the extent of electron scattering by the spins of the Pr sublattice is reduced. Furthermore, the spin moments of the Pr sublattice can indirectly affect the electron scattering by the Mn sublattice because the conduction electrons around the Fermi level are mainly represented by the Mn atoms[15] and because the spin moments of a Pr layer interact with those of its adjacent Mn layer. Due to the interactions of the Pr spins with the Mn spins, the ferromagnetic ordering in each Mn layer may not be complete, thereby leading to spin fluctuation. The spins of each Mn-layer tend to become ferromagnetically ordered above ∼50 K with or without an

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applied external field. However, this tendency is counteracted by an antiferromagnetic coupling of the spins of each Mn layer with disordered spins of its adjacent Pr layers. Therefore, the field-induced alignment in the Pr sublattice would strengthen the ferromagnetic ordering of the Mn lattice and hence enhance the negative magnetoresistance. Thus, the large negative magnetoresistance of $PrMnSi_2$ in the ferromagnetic region suggests a substantial exchange coupling between the Mn and Pr atoms in the adjacent layers. The occurrence of such a coupling is also evidenced by the magnetic structure determined at 4.2 K. It shows the spins of adjacent Mn layers to become antiferromagnetically ordered when the spins of each of the adjacent Pr layers are ferromagnetically ordered below ~50 K. In the study of $Eu_{14-x}A_xMnSb_{11}$ (A = Ca, Sr),[9] the coupling between the rare-earth and Mn atoms was identified as the origin of its CMR.

3.3. Resistivity Hysteresis. The electrical resistivity of $PrMnSi_2$ at zero field exhibits a strong thermal hysteresis. As shown in Figure 4a, the resistivity of the cooling cycle is lower than that of the warming cycle. The zero-field resistivity vs temperature curve for the cooling cycle is similar to the resistivity vs temperature curve of the warming cycle under $H = 2-3$ T shown in Figure 2. The higher resistivity on the warming cycle can be rationalized by supposing antiferromagnetic interactions between the spins of adjacent Pr and Mn layers. As already suggested, the latter disfavor not only a complete disordering of the Pr magnetic moments but also a complete ferromagnetic ordering of the Mn magnetic moments. This implies a lower magnetic susceptibility for the warming cycle than for the cooling cycle. This was indeed observed in the thermal hysteresis of the magnetic susceptibility measured at a low field in our previous study.[15] The thermal hysteresis becomes weaker when a magnetic field is applied (Figure 4b), and this is understandable because the extent of antiferromagnetic coupling between adjacent Mn and Pr layers would become reduced under field. The hysteresis almost disappears at 4 T, and it will disappear completely above 5 T because no hysteresis is observed in the magnetic susceptibility at 5 T.[15]

4. Concluding Remarks

The resistivity vs temperature curves of $PrMnSi_2$ exhibit a significant hysteresis in the absence and presence of an applied magnetic field not only below ~50 K where $PrMnSi_2$ becomes antiferromagnetic but also above ~50 K where $PrMnSi_2$ becomes ferromagnetic. The magnetoresistance vs temperature curves of $PrMnSi_2$ determined at magnetic fields up to ~3 T show three peaks at the temperatures where the three magnetic phase transitions were found to occur. The magnetoresistance phenomena of $PrMnSi_2$ are explained by considering how the scattering of the electrons at the Fermi level is reduced under magnetic field. Our analysis indicates that the negative magnetoresistance above ~50 K is related to a field-induced spin alignment in the Pr sublattice and a concomitant, stronger ferromagnetic ordering of the Mn sublattice. The negative magnetoresistance below ~50 K is caused by both a field-induced spin alignment in the Pr sublattice and a field-induced antiferromagnetic-to-ferromagnetic transition in the Mn sublattice. The magnetoresistance and the resistivity hysteresis of $PrMnSi_2$ indicate the presence of a substantial antiferromagnetic coupling between adjacent Mn and Pr layers.

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