Evidence for spin-glass state in nonmagnetic atom disorder compound Pr$_2$AgIn$_3$

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Abstract. A systematic investigation of magnetic properties has been performed on intermetallic compound Pr$_2$AgIn$_3$, which crystallizes in a disordered hexagonal CaIn$_2$-type structure. We present the experimental results of ac and dc susceptibility, magnetization, magnetic relaxation, specific heat and electrical resistivity measurements. The results provide clear evidence for the formation of spin-glass state in Pr$_2$AgIn$_3$ below a spin freezing temperature $T_f \approx 3.7$ K accompanied with a short-range magnetic order. The spin-glass behavior of Pr$_2$AgIn$_3$ is discussed and compared with that observed for the isostructural compounds Ce$_2$AgIn$_3$ and Nd$_2$AgIn$_3$ as well as other 2:1:3 spin-glass materials. The spin-glass state in Pr$_2$AgIn$_3$ can be considered to originate from the continued site randomness of the non-magnetic elements, Ag and In, which introduce the random distribution of the RKKY interactions.

1. Introduction

Ternary intermetallic compounds with a general formula $R_2TX_3$ ($R$=U or rare-earth element, $T$=transition 3d, 4d and 5d element, $X$=Ga, In, Si, Ge) have been the subjects of intensive studies during the past years because of their intriguing physical properties. Many members of these materials are reported to crystallize in the “binary-type” structure, e.g., the AlB$_2$-type structure (space group $P6/mmm$), the CaIn$_2$-type structure (space group $P6_3/mmc$), or derivatives of those hexagonal structures [1]. The interest in these compounds stems from the distribution of the $R$, $T$ and $X$ elements on the crystallographic sites with a complete order of magnetic $R$ atoms on the Al/Ca site and a random distribution of the transition metal $T$ and $X$ atoms on the B/In site of the AlB$_2$-/CaIn$_2$-type structure. Because the d/p electronic states of ligands are considered to affect the magnetic interactions of $R_2TX_3$ compounds strongly, the random distribution of $T$ and $X$ elements can be expected to cause some anomalous magnetic properties such as spin-glass (SG) behavior. This has indeed been confirmed by recently experimental results, e.g., the SG behavior in Ce$_2$CuX$_3$ ($X$=Si [2] and Ge [3]) and U$_2$TSi$_3$ ($T$=Pd [4], Pt [5], Au [6] and Rh [7]); the coexistence of long range magnetic order state and SG state in Tb$_2$PdSi$_3$ [8] and Tb$_2$CuIn$_2$ [9]; and the complex magnetic ordering in Nd$_2$CuSi$_3$ [10] and $R_3$PdSi$_3$ ($R$=Eu [11], Dy, Ho, Er [8], Gd [12]), etc. However, in many cases, a clear consensus regarding the magnetic nature is still elusive. In particular, it is a common belief that competing
between ferromagnetic and antiferromagnetic near-neighbour interactions caused by randomly varying bond angles and interatomic distances are mainly responsible for the formation of SG state in amorphous or diluted metallic SG materials. Intermetallic compounds \( R_2TX_3 \), however, are crystallographically ordered substances. In such systems, the origin of SG behavior is evidently different from that in amorphous or diluted metallic SG systems, and is not elucidated theoretically so far. To clarify the mechanism of magnetic interactions systematic experimental data on other \( R_2TX_3 \) compounds are necessary. Recently, we have been paying special attention to a new family of the \( 2:1:3 \) compounds, namely \( R_2AgIn_3 \) (\( R=\)rare-earth element). According to neutron diffraction, the Tb compound is the only example in this series to show long-range magnetic order \([13]\) with the Néel temperature \( T_N=42 \) K. On the other hand, experimental measurements of thermal, magnetic and transport properties reported for \( R_2AgIn_3 \) reveal the canonical SG behavior for \( R=\)Ce \( (T_f=1.8 \) K) \([14]\), SG-like behavior for \( R=\)Tm \( (T_f=3.2 \) K) and SG behavior with short-range antiferromagnetic order for \( R=\)Nd \( (T_f=12.6 \) K) \([15]\). In this paper, we present the results of ac and dc susceptibility, magnetization, magnetic relaxation, electrical resistivity and specific heat measurements of polycrystalline \( Pr_2AgIn_3 \). Our results provide clear evidence for the existence of SG state in \( Pr_2AgIn_3 \), and suggest that the occurrence of SG behavior is accompanied with the formation of short-range magnetic order.

2. Experimental

The polycrystalline sample of \( Pr_2AgIn_3 \) was prepared by melting appropriate amounts of the constituent elements in an arc furnace under purified argon atmosphere. The sample was then wrapped into tantalum foil and annealed in evacuated silica tube at 750 °C for two weeks. X-ray powder diffraction was performed at room temperature with CuKα radiation. The samples used in the experiments are small pieces cut from the annealed button. The ac and dc susceptibility, low-field magnetization and magnetic relaxation were measured between 1.8 and 300 K in magnetic fields up to 10 kOe using a SQUID magnetometer. High-field magnetization experiments at 2.7 K were carried out using an Oxford Instruments VSM 12 T magnetometer in magnetic fields up to 110 kOe. The adiabatic heat pulse method was employed for specific heat measurements over the temperature range between 1.7 and 20 K. Electrical resistivity measurements were performed between 3.2 and 284 K using a standard four-terminal DC method.

3. Results

From the results of powder x-ray diffraction, the annealed \( Pr_2AgIn_3 \) sample was found to be almost single-phased. The diffraction lines can be indexed based on the disordered hexagonal CaIn2-type structure model (space group \( \text{P6}_3/mmc \)) with Pr atoms on 2b sites \((0, 0, 1/4)\) and Ag and In atoms statistically distributed over the \( 4f \) sites \((1/3, 2/3, z)\) with \( z=0.465 \) \([13]\). The determined room-temperature lattice constants are \( a=4.872(3) \) Å and \( c=7.594(5) \) Å.

The temperature dependence of the zero field-cooled dc susceptibility \( \chi_{ZFC} (=M_{ZFC}/H) \) of \( Nd_2AgIn_3 \) measured in a field of \( H=100 \) Oe is shown in Fig. 1. Above 20 K the observed \( \chi_{ZFC}(T) \) behavior can be well described by the modified Curie-Weiss law \( \chi=\chi_0+C/(T-\theta_p) \) (solid line in the insets of Fig. 1). Where \( C \) is the Curie constant, \( \theta_p \) the paramagnetic Curie temperature and \( \chi_0 \) denotes temperature-independent contributions such as core diamagnetism, Landau diamagnetism and Pauli paramagnetism. From the fit, we obtain the values of \( \chi_0=3.49 \) \( \mu_0 \)Pr, \( \theta_p=–4.9 \) K, and \( \chi_0=2.08\times10^{-6} \) emu/g. The value of effective magnetic moment \( \mu_{eff}=3.49 \) \( \mu_0 \)Pr is close to the value of 3.58 \( \mu_0 \) expected for free-ion \( Pr^{3+} \) in the \( J=4 \) Hund’s rule ground state indicating the \( 4f \) electrons are almost localized within the
Pr atoms. At low temperatures, a sharp peak is observed near $T_f=3.7$ K indicating some kind of magnetic phase transition near this temperature.

In order to characterize the nature of this transition, the field-cooled (FC) and zero field-cooled (ZFC) susceptibilities in various applied fields were measured around $T_f$. As shown in Fig. 2, there is no difference between the FC and ZFC curves in the paramagnetic state, and the magnetic transition peak can be observed only in the $\chi_{ZFC}(T)$ curve at the strongly field dependent temperature $T_f(H)$ that closes to 3.7 K in low field. Moreover, irreversible magnetism manifesting as the bifurcation between the FC and ZFC curves appears below a characteristic temperature $T_{ir}(H)$. With increasing $H$, the peak in $\chi_{ZFC}(T)$ becomes broader and its height decreases, while both $T_f(H)$ and $T_{ir}(H)$ shift toward lower temperatures. The strong field dependence of the peak position $T_f$ in $\chi_{ZFC}(T)$ curve and the evident irreversible magnetism below $T_{ir}$ are the typical features of SG system. Note that $T_{ir}$ for a canonical SG is equals to $T_f$ even in low magnetic field. For Pr$_2$AgIn$_3$, however, $T_{ir}$ is clearly higher than $T_f$ in applied field below 1 kOe suggesting the observed features are not simple SG behaviors.

The irreversible magnetism described above indicates the nonequilibrium feature of the low-temperature magnetic states in Pr$_2$AgIn$_3$. Thermodynamically, such nonequilibrium states directly relate to slow dynamics and could also lead to the remanence phenomenon in field dependence of magnetization and long-time magnetic relaxation effect. High-field magnetization $M(H)$ of Pr$_2$AgIn$_3$ measured at 2.7 K is illustrated in Fig. 3. It is clear that $M(H)$ curve does not saturate up to 110 kOe, and when $H$ is returned from 110 kOe to zero, remanent magnetization of about 0.13 emu/g is detected. From the hysteresis loop we determine the coercive field $H_c$ of Pr$_2$AgIn$_3$ to be 230 Oe at 2.7 K. Magnetic relaxation effect of Pr$_2$AgIn$_3$ was studied at 3 K by measured the magnetization $M$ as a function of time $t$ in zero and 400 Oe applied fields, the results are displayed in the insets of Fig. 3. Before the measurement, the sample was first ZFC from 50 K to 3 K, then, in the case of inset of Fig. 3(a) a magnetic field of 5 kOe was applied for 5 min and switched off at $t=0$, and in the case of inset of Fig. 3(b) a field of 400 Oe was applied at $t=0$. In both cases, the decay of $M(t)$ is remarkably slow, nonzero remanence in zero field [inset of Fig.3(a)] and unsaturated magnetization in 400 Oe [inset of Fig.3(b)] can be observed even after waiting for 1h. Using a logarithmic function, $M(t) = M_0 - S \ln(t + t_0)$, the obtained relaxation behaviors shown in the insets of Fig. 3 can been fitted very well over...
the full time range studied with three $H$- and $T$-dependent fitting parameters: initial zero-field magnetization $M_0$, magnetic viscosity $S$ and characteristic time $t_0$. The best fitting results obtained by using the least-squares method are shown by the solid lines in the insets of Fig. 3 with positive and negative $S$ values in zero field and 400 Oe, respectively.

It is well known that the characteristic features of irreversible magnetism and magnetic relaxation effect can be observed not only for SG material, but also for long-range magnetic order system with high magnetic anisotropy [16]. For Pr$_2$AgIn$_3$, the existence of long-range spatial magnetic ordering can be excluded by our specific heat and electronic resistivity measurements. Figure 4 illustrates the temperature dependence of specific heat $C(T)$ of Pr$_2$AgIn$_3$. Although it is not easy to separate the magnetic contribution $C_m$ from the total specific heat (consisting of vibrational, electronic and magnetic parts) accurately, the absence of dramatic change in $C(T)$ around $T_f \sim 3.7$ K indicates no sharp peak in $C_m(T)$ and thus excludes the existence of long-range magnetic ordering at $T_f$. At low temperatures, the $C/T$ vs. $T^2$ plot shown in the inset of Fig. 4 yields for $T \rightarrow 0$ K a $\gamma$ value (the specific heat coefficient of $T$-linear term) of 375 mJ (mole-Pr)$^{-1}$ K$^{-2}$ for Pr$_2$AgIn$_3$ much larger than that of a normal metal. Note that $C(T)$ curve shows a broad bend around 5 K just above $T_f$ similar to that observed for Ce$_2$AgIn$_3$ [14] and Nd$_2$AgIn$_3$ [15], and different from that observed for U$_3$PdSi$_3$ [4]. This broad bend may be due to the formation of magnetic cluster (short-range magnetic order). Thus in addition to the influence of random distribution of Ag and In atoms (which usually originates the large $\gamma$ value in nonmagnetic atom disorder system [17]), the short-range magnetic correlation could also contribute to the observed large $\gamma$ value considering the magnetic cluster formed at sufficiently low temperature.

Figure 5 gives the results of electrical resistivity [$\rho(T)$] measurement for Pr$_2$AgIn$_3$ between 3.2 and 284 K. $\rho(T)$ shows metallic conductivity with some negative curvature between 50 and 150 K, which may be resulted from crystal field interaction and/or s-d interband scattering of conduction electrons [18]. As clearly shown in the inset of Fig. 5 in an expanded scale, no anomaly can be detected at $T_f \sim 3.7$ K, which provides a new evidence for the absence of long-range magnetic ordering in Pr$_2$AgIn$_3$.

In order to confirm the SG effects and characterize the spin freezing state, we have also performed an ac susceptibility measurement on the Pr$_2$AgIn$_3$ sample at various frequencies. Figure 6 shows the temperature dependence of the real component ($\chi_{ac}'$) of the ac susceptibility of Pr$_2$AgIn$_3$ between 3.2 and 5.5 K at the frequency range $0.1 \leq \omega / 2 \pi \leq 1000$ Hz. $\chi_{ac}'$ exhibits a pronounced maximum with amplitude and position depending on the frequency of the applied magnetic field. At a frequency of 0.1 Hz, the cusp in $\chi_{ac}'$ appears at $T_f = 3.7$ K, which shifts to 4.2 K at $\omega / 2 \pi = 1000$ Hz. Although the value of the imaginary component ($\chi_{ac}''$, not shown here) is much smaller than that of $\chi_{ac}'$ and has relatively large
error, a cusp in $\chi_{ac}$ curve, which shifts to higher temperatures with frequency, is also observed clearly. These results provide important evidence for the formation of SG state in Pr$_2$AgIn$_3$. For convenience, in this paper we define the spin freezing temperature $T_f$ as the peak temperature in $\chi_{ac}'(T)$ curve. Similar frequency shift of the ac susceptibility maximum is also observed for Ce$_2$AgIn$_3$ [14] and Nd$_2$AgIn$_3$ [15]. The initial frequency shift $\delta T_f$ calculated as $\delta T_f = \Delta T_f / (T_f \Delta \log \omega)$ is 0.031 comparable to the typical values (from a few thousandths to a few hundredths) for most SG materials [19]. In order to further identify the nature of spin freezing state, the Vogel and Fulcher empirical law [20], $\omega = \omega_0 \exp\left[-E_a / k_B(T_f - T_0)\right]$, and the conventional critical slowing down model [21], $\tau_{\text{max}} = \tau_0[(T_f - T_0)/T_0]^{-\nu}$, were used to analyze the frequency dependence of ac susceptibility. Assuming $\omega_0/2\pi = 10^{10}$ Hz, typically taken in the SG systems [19, 22], we obtained the best fitting results as shown by the solid lines in the insets of Fig. 6 with the values of fitting parameters: activation energy $E_a/k_B = 20.25$ K, characteristic temperature $T_0 = 2.98$ K, static freezing temperature $T_f = 3.38$ K and critical (dynamical) exponent $\nu = 11.75$.

4. Discussion and conclusions

It is well known that some typical properties for SG material are (1) frozen-in magnetic moments below a freezing temperature $T_f$ and hence a cusp-like anomaly in the frequency-dependent ac susceptibility around $T_f$; (2) irreversible magnetism behaving as the difference between FC and ZFC magnetization below $T_f$; (3) lack of periodic long-range magnetic order and (4) remanence and magnetic relaxation on macroscopic time scales after changing the applied magnetic field below $T_f$ [23]. All these features are observed in Pr$_2$AgIn$_3$ in the present work, which can be considered as the evidences for the formation of SG state in this system.

The existence of frustration and randomness are the necessary conditions for SG state [23]. It means that there must be a competition between ferromagnetic and antiferromagnetic interactions so that no single configuration of the spins is uniquely favored by all the interactions, and the distribution of ferromagnetic and antiferromagnetic interactions between magnetic atoms must be at least partially random. Ternary intermetallic compound Pr$_2$AgIn$_3$ crystallizes in the CaIn$_2$-type structure, which consists of layers of magnetic Pr atoms alternating with non-magnetic Ag-In layers along the c-axis. Within one magnetic layer Pr atoms form triangles of nearest neighbours. The statistical disorder of the Ag and In atoms within the Ag-In layers could vary the electronic environment around the Pr ions, lead to the random distribution of the RKKY interactions, and thus induce the formation of frustrated magnetic moments of Pr ions and/or Pr clusters. Below a critical temperature $T_f$ (~3.7 K, freezing temperature) the frustrated magnetic moments could be frozen in random directions forming the SG state. In fact, the neutron diffraction study for Tb$_2$AgIn$_3$ has confirmed the existence of competition between ferromagnetic and antiferromagnetic interactions within Tb layers [24]. Similar competing magnetic interactions and thus frustrated magnetic moments are naturally expected in Pr$_2$AgIn$_3$ due to the isostructuralism.

As described above, the observed magnetic behavior of Pr$_2$AgIn$_3$ suggests the formation of SG state with short-range magnetic order in this compound similar to that in Ce$_2$AgIn$_3$ and Nd$_2$AgIn$_3$. For Nd$_2$AgIn$_3$, the FC susceptibility ($\chi_{FC}$) does not show tendency of saturation as $T$ is lowered below $T_f$ (~13 K), in contrast, slow decrease of $\chi_{FC}$ can be observed down to 7 K. In addition, the $\chi(T)$ curve of Nd$_2$AgIn$_3$ illustrates an upturn below about 25 K (not published). These properties indicate the antiferromagnetic nature of the magnetic coupling within magnetic cluster. Thus Nd$_2$AgIn$_3$ is categorized as a SG with short range antiferromagnetic order. In the present case, however, the $\chi_{FC}(T)$ curve of Pr$_2$AgIn$_3$ does not decrease below $T_f$ even in a very low field (see Fig. 2), while the low field $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves separate from each other at the temperature $T_0 > T_f$ as usually observed in ferromagnetic cluster-glass systems. Moreover, there is no upward tendency can be observed in $\chi(T)$ curve down to the lowest temperature measured (see Fig. 5). These features are significantly different with that observed for Nd$_2$AgIn$_3$, suggesting the ferromagnetic-like nature of the short-range magnetic order within the magnetic cluster in Pr$_2$AgIn$_3$ in spite of the negative paramagnetic Curie temperature.
Of course, to confirm the formation of SG state in Pr\textsubscript{2}AgIn\textsubscript{3} from different point of view, further experimental researches including non-linear susceptibility measurement (which is expected to show the negative divergence at $T_f$) are necessary.

In conclusion, ac and dc susceptibility, magnetization, magnetic relaxation, specific heat and electrical resistivity measurements were performed for Pr\textsubscript{2}AgIn\textsubscript{3}. This compound was found to undergo a SG transition with a freezing temperature $T_f \sim 3.7$ K. The lack of anomaly in both specific heat and electrical resistivity around $T_f$, the up-shift of the ac susceptibility peak with increasing frequency, the down-shift of the dc susceptibility peak with increasing field, the long-time magnetic relaxation effect and the low temperature irreversible magnetism can be considered as the evidence for the formation of SG state. To characterize the spin freezing state of this system, the static spin freezing temperature $T_S$, critical exponent $\nu z$ and activation energy $E_a$ are determined from dynamical analyses of the ac susceptibility data. In addition, FC-ZFC susceptibilities and specific heat measurements suggest the existence of magnetic clusters with evident influence on the magnetic properties. Thus it seems to be appropriate to consider Pr\textsubscript{2}AgIn\textsubscript{3} as a SG with short-range magnetic order.

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