Magnetic Phase Transition in $Pd_xCo_yO_2$

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Abstract

$PdCoO_2$, which crystallize in the delafossite-type structure (space group $R\overline{3}m$), shows a high metallic conductivity and Pauli-type paramagnetism. The composition modified compounds $Pd_xCo_yO_2$(x=0.72, y=0.68) were prepared by matathetical reaction, characterized by X-ray powder diffraction (XPD) and inductively coupled plasma spectroscopy (ICPS). The magnetic properties have been studied by means of dc magnetic susceptibility and heat capacity. Two cusps were seen in the ZFC curve, regarded as spin-glass transition points, suggest that the longitudinal ($\chi_{\parallel}$) and transverse ($\chi_{\perp}$) components of spins freeze independantly. The experimental results are explained by mean-field theories for Heisenberg spin-glass with local uniaxial anisotropy.

Key words: $PdCoO_2$; delafossite ; triangular lattice ; magnetic phase transition ; spin-glass

Low temperature properties of diluted noble metal alloys in the spin-glass regime have received substantial attention over the past forty years. $PdCoO_2$, which crystallize in the delafossite-type structure (space group $R\overline{3}m$), shows a high metallic conductivity and Pauli-type paramagnetism [1–7]. These crystals are physically attractive because the structure has a layered triangular lattice which causes magnetic spin frustration. Hasegawa et al. has been reported that manganese substitution on $PdCoO_2$ shows curious magnetic behavior like a spin-glass [8]. The occurence of a spin-glass phase in a pure substance is unusual but is known in cases where magnetic frustration is strong and some sort of site randomness of magnetic ions occures, or if a sufficient defect concentrarion arises [9]. From this point of view, sufficient defects in $PdCoO_2$ may well exhibit significant magnetic ion site randomness or defect concentrarion as well as frustration and low dimensionality of magnetic interaction. In this article, we report the synthesis and characterization of composition modified compound $Pd_xCo_yO_2$, and its curious magnetic behavior.

The polycrystalline compound $Pd_xCo_yO_2$ were prepared by metathetical reaction, detailed procedure has been already described elsewhere [1,2,4–6]. The obtains products were carefully leaching out by-products, characterized with an X-ray powder diffraction (RAD-C, Rigaku) and the inductively coupled plasma spectroscopy (ICPS-5000, Shimazu). The XPD pattern for the $Pd_xCo_yO_2$ was refined by Rietveld analysis [12], and all the intensity peaks were assigned to $PdCoO_2$ delafossite-type structure without any impurity phases. From the results of ICPS, the chemical composition of the compound was determined to be $Pd_{0.72}Co_{0.68}O_2$. Magnetic susceptibility (χ) measurements were carried out in a SQUID magnetometer using a scan length of 3cm to avoid inhomogenity in zero-field-cooled (ZFC) and field-cooled (FC) mode. The heat capacity (C_p) was measured in a Physical-Property-Mesurement-System (PPMS, Quantum Design) using the standard thermal relaxation techniques.

Fig.1 shows the magnetization for both the ZFC and FC processes in fields from 100 to 10 kOe at tem-

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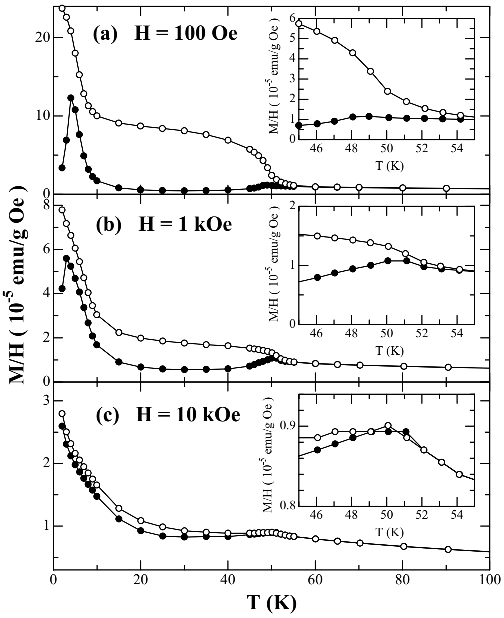

Fig. 1. Magnetization on the M/H vs. T plots recorded in ZFC(•) and FC(∘) histories; (a)100 Oe, (b) 1 kOe and (c) 10 kOe. The insets highlight the thermomagnetic irreversibility.

perature between 2 and 100K. The deviation of FC from ZFC curve appears below 55K, indicating the occurence of an irreversible effect of magnetization, and two cusps (the broad cusp at ∼50K and the sharp cusp at ∼3K) are seen in the ZFC curve in Figs.1(a) and (b). It can be seen that both cusps become smaller and broader with increasing field, and disappears for fields above 10 kOe. This further implies that these cusps likely relate to a spin-glass.

We have studied the thermoremanent magnetization (TRM) in $Pd_{0.72}Co_{0.68}O_2$ as a function of temperature in some detail. A pronounced long-term decay was observed, commonly seen in spin-glasses, full particulars of which will appear elseshere. Therefore, these cusps can be regarded as two spin-glass transition points denoted by $T_{\rm g1}$(∼3K) and $T_{\rm g2}$(∼50K).

Similar results have been found for $Mn_{1-x}Ni_xSb$, ZnMn, MgMn, and CdMn alloys [10,11], these behaviors indicate that two successive transitions occur in these systems as was suggested by mean-field theories for Heisenberg spin-glass with local uniaxial anisotropy, including consideration of replica-symmetry breaking [13,14]. According to this theory, there should be two successive transitions, from the paramagnetic state to the longitudinal-ordering state and then at lower temperatures to a mixed phase (longitudinal-transverse-ordering state). The occurence of two independent cusps suggests that the longitudinal ($\chi_\parallel$) and transverse ($\chi_\perp$) components of spins freeze independantly. As temperature is lowered from the paramagnetic state, $\chi_\parallel$ shows cusp at $T_{\rm g2}$, while $\chi_\perp$ still increases smoothly through $T_{\rm g2}$. On further decrease of the temperature, $\chi_\perp$ also shows a sharp maximum at $T_{\rm g1}$.

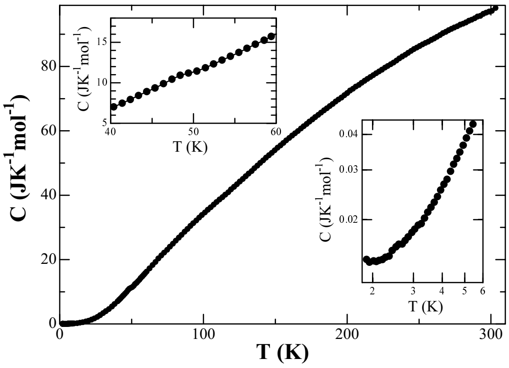

Fig. 2. Temperature dependence of the heat capacity of $Pd_{0.72}Co_{0.68}O_2$. The insets highlight two spin-glass transition points ($T_{\rm g1}$ and $T_{\rm g2}$).

The heat capacity ($C_{\rm p}$) of $Pd_{0.72}Co_{0.68}O_2$ measured between 1.8K and 300K is shown in Fig.2. If there is some kind of phase change at $T_{g1,2}$, then a clear indication would be expected in the heat capacity, but this displays a broad anomaly at $T_{g1,2}$. This result also suggests the existence of spin-glass transitions [15].

Two conditions must be fulfilled for spin-glass formation: randomness and frustration. Although we have randomness in Co triangular layer, it is speculative to assign where the magnetic moment is located and what types of interactions would produce frustration. For further quantitative discussion for the magnetic state, we need longitudinal and transverse magnetic susceptibilities measured on single crystals.

In conclusion, the effect of defects injection on magnetic properties in $Pd_{0.72}Co_{0.68}O_2$ polycrystalline has been studied. Two cusps were seen in the ZFC curve, regarded as spin-glass transition points denoted by $T_{\rm g1}$ and $T_{\rm g2}$. The occurence of two independent cusps suggests that the longitudinal ($\chi_\parallel$) and transverse ($\chi_\perp$) components of spins freeze independantly. It is explained by mean-field theories for Heisenberg spin-glass with local uniaxial anisotropy.

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