Magnetic Phase Transition in Pd$_x$Co$_y$O$_2$

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Abstract

PdCoO$_2$, which crystallize in the delafossite-type structure (space group $Rar{3}m$), shows a high metallic conductivity and Pauli-type paramagnetism. The composition modified compounds Pd$_x$Co$_y$O$_2$($x=0.72$, $y=0.68$) were prepared by metathetical 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 independently. 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 $Rar{3}m$), 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 occurrence 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 occurs, or if a sufficient defect concentration arises [9]. From this point of view, sufficient defects in PdCoO$_2$ may well exhibit significant magnetic ion site randomness or defect concentration as well as frustration and low dimensionality of magnetic interaction. In this article, we report the synthesis and characterization of composition modified compound Pd$_x$Co$_y$O$_2$, and its curious magnetic behavior.

The polycrystalline compound Pd$_x$Co$_y$O$_2$ 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). The XPD pattern for the Pd$_x$Co$_y$O$_2$ 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 ($\chi$) measurements were carried out in a SQUID magnetometer using a scan length of 3cm to avoid inhomogeneity 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-
longitudinal (occurrence of two independent cusps suggests that the phase (longitudinal-transverse-ordering state). The state and then at lower temperatures to a mixed paramagnetic state to the longitudinal-ordering symmetry breaking [13,14]. According to this the-axial anisotropy, including consideration of replica-theories for Heisenberg spin-glass with local uni-
haviors indicate that two successive transitions oc-
ZnMn, MgMn, and CdMn alloys [10,11], these be-
spins freeze independantly. As temperature is lowered

\[ \chi (T) \sim \frac{1}{T^3} \]

Two conditions must be fulfilled for spin-glass for-
we need longitudinal and transverse magnetic suscept-
In conclusion, the effect of defects injection on mag-
polycrystalline has two types of interactions would produce frustration. For
the paramagnetic state, \( \chi_\parallel \) shows cusp at \( T_{g2} \),
while \( \chi_\perp \) still increases smoothly through \( T_{g2} \). On further decrease of the temperature, \( \chi_\perp \) also shows a sharp maximum at \( T_{g1} \).

The heat capacity (\( C_p \)) of Pd\(_{0.72}\)Co\(_{0.28}\)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 form-
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 mag-
properties in Pd\(_{0.72}\)Co\(_{0.28}\)O\(_2\) polycrystalline has been studied. Two cusps were seen in the ZFC curve, regarded as spin-glass transition points denoted by \( T_{g1} \) and \( T_{g2} \). The occurrence of two independent cusps sug-
gests 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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References