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Doping through the percolation limit in $GeNi_{2-x}Co_xO_4$

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Abstract

The solid solutions $GeNi_{2-x}Co_xO_4$ have been prepared to examine the difference in ground states between integer and non-integer spins on the corner-shared tetrahedra lattice. It is found that there is a change in the evolution of the Weiss constant, and the magnetic transition temperatures near the percolation limit for the pyrochlore lattice. Substitution with Ni^{2+} results in a filling of the t_{2g} orbitals and acts like a non-magnetic impurity. The sensitivity of the $GeNi_2O_4$ magnetic ground state to impurities is demonstrated by a change in sign of the Weiss constant for very small Co^{2+} doping (5%). A third magnetic transition in $GeNi_2O_4$ at $T \sim 11$ K, in addition to previous transitions at $T_{N1} = 12.1$ K and $T_{N2} = 11.5$ K, is noted through dc susceptibility measurements. Evidence for phase separation in $GeNi_2O_4$ is observed.

1. Introduction

Materials exhibiting geometric frustration (GF) have been the topic of much recent interest. The rich physical properties are due to large ground-state degeneracies. Spinels and pyrochlores are two typical crystal structures that show GF due to the three-dimensional networks of corner-sharing tetrahedra. Many spinel systems have been studied with half-integer spins, such as $ZnCr_2O_4$ ($S = 3/2$) and $ZnFe_2O_4$ ($S = 5/2$) [1, 2]. In these systems, the frustrations are relieved by a change in structural symmetry at the magnetic ordering temperature. The absence of such a structural transition in some integer spin systems has led to speculation about fundamentally different ground states for integer and half-integer spins. As an analogy, in the case of one-dimensional antiferromagnets, spin-Peierls transitions are not observed in spin-one chains due to the presence of a Haldane gap [3]. The discovery of an analogous gapped state in integer spin three-dimensional frustrated lattices is driving future research into the characterization of these systems. Several theoretical papers point out that the excitations

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of integer Heisenberg spins might differ considerably from those of half-integer spins on the pyrochlore lattice [4, 5]. In pyrochlore antiferromagnets, for example, a series of Néel phases accompanied by a rich spin-wave spectrum is predicted for $S = 1$ [6].

$GeNi_2O_4$ is a spinel with integer spin ($S = 1$). It has the normal spinel structure, with Ni^{2+} ($3d^8$) ions at the vertices of corner-sharing tetrahedra (the spinel B site). Former studies have revealed a two-step magnetic transition at $T_{N1} = 12.13$ K and $T_{N2} = 11.46$ K, and did not reveal a structural transition at T_{N1} and T_{N2}, which is significantly different from the spinels with half-integer spins [7]. Recently, a muon-spin relaxation (μ^+SR) study of $GeNi_2O_4$ showed evidence for phase separation into short-range-and long-range-ordered regions at low temperature [8]. Moreover, a cusp appears in the specific heat at 11 K, which implies that a third magnetic phase transition may be present in $GeNi_2O_4$ [9]. On the other hand, $GeCo_2O_4$ with a half-integer spin ($S = 3/2$) magnetic sublattice undergoes a lattice distortion at the single magnetic transition $T_N = 20$ K [10].

Former studies have been focused on $GeNi_2O_4$ and $GeCo_2O_4$ [11, 12] to note the different magnetic behaviours between them, but how the magnetic phase develops from $S = 1$ to $3/2$ is still not clear. In this paper, we substitute Co^{2+} for Ni^{2+} in single-phase samples of $GeNi_{2-x}Co_xO_4$ ($0.0 \leqslant x \leqslant 2.0$) in order to elucidate how the magnetic phase develops with changing x. Detailed magnetization measurements also are performed to study the phase separation and a possible third magnetic phase transition.

2. Experimental details

Polycrystalline samples of $GeNi_{2-x}Co_xO_4$ ($0.0 \leqslant x \leqslant 2.0$) were prepared by standard solid-state reactions. Mixtures of GeO_2, NiO, and CoO in the appropriate ratios were ground and calcined in air at around 1100–1150 °C for 6 h. All samples were single-phase, as determined by powder x-ray diffraction (XRD) with a Cu Kα source. Magnetic susceptibility measurements were made with a Quantum Design dc superconducting quantum interference device (SQUID) magnetometer from 2 to 300 K in fields up to 4.5 T.

3. Results

Lattice parameters obtained from powder XRD for the cubic system $GeNi_{2-x}Co_xO_4$ with $Fd\bar{3}m$ structure indicate a complete solid solution over the range ($0.0 \leqslant x \leqslant 2.0$). Figure 1 shows the Rietveld refinement for the $GeNi_2O_4$ XRD pattern with $R_p = 8.7$, $R_{wp} = 13.2$ and $\chi^2 = 2.3$ using the program FullProf. With increasing Co content, the lattice parameter increases linearly (see the inset of figure 1).

Figure 2 shows the temperature dependences of the molar magnetic susceptibility $\chi(T)$ and its inverse $1/\chi(T)$ measured with $H = 100$ Oe by the zero field cooling process. All samples show a maximum at around 20 K (14 K $< T_N <$ 23 K), and with increasing Co content the maximum shifts to higher temperature.

Figure 3(a) shows the detail of the susceptibility around the magnetic transition T_N for $GeNi_2O_4$. χ begins to drop at $T_N \approx 14$ K, followed by a two-step transition at $T_{N1} = 12.1$ K and $T_{N2} = 11.4$ K, which are determined by the position of a sharp peak in $d\chi/dT$. It is noteworthy that the $d\chi/dT \sim T$ curve shows a prominent cusp at $T_3 = 11.1$ K, which follows the transition at T_{N2}. The $d\chi/dT \sim T$ curves measured at different magnetic fields are shown in figure 3(b). With increasing magnetic field up to $H = 4$ T, T_{N1} does not change and T_{N2} only shows a slight decrease. The intensity of the peaks around T_{N1} and T_{N2} both decrease with increasing field. The cusp for T_3 shows more complicated behaviour with changing field. With $H < 1$ T, the intensity of the cusp increases with increasing field and develops to a peak at

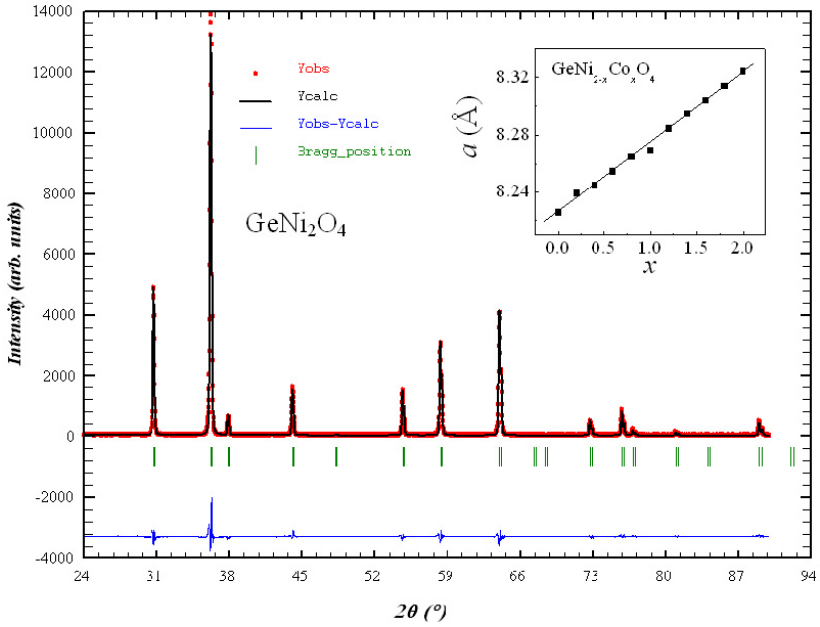

Figure 1. Room-temperature XRD pattern for $GeNi_2O_4$ (dots). The solid curve is the best fit from the Rietveld refinement using FullProf. The bottom curve shoes the difference between the measured and calculated intensities. Inset: variation of lattice parameter with x for $GeNi_{2-x}Co_xO_4$.

(This figure is in colour only in the electronic version)

$H = 1$ T; with $H > 1$ T, the intensity decreases with increasing field and the cusp disappears at around $H = 3$ T. At the same time, T_3 decreases with increasing field.

Figure 4 shows the $d\chi/dT \sim T$ curves for $GeNi_{2-x}Co_xO_4$ measured with $H = 100$ Oe. Several features are noteworthy: (i) only for $GeNi_2O_4$ does the $d\chi/dT \sim T$ curve show a cusp at T_3; (ii) for $x \leqslant 0.6$, T_{N1} and T_{N2} both increase, but the intensity of the peaks decreases with increasing x; (iii) for $x > 0.6$, the peak for T_{N1} disappears, but the peak for T_{N2} is persistent until $x = 1.8$; (iv) the $d\chi/dT \sim T$ curve measured with $H = 4.5$ T for $GeNi_{1.2}Co_{0.8}O_4$ shows no peak.

Figure 5(a) shows the $d\chi/dT \sim T$ curves for $GeNi_{1.6}Co_{0.4}O_4$ measured with different fields. The effect of magnetic field on T_{N1} and T_{N2} for this sample is obviously stronger than that for $GeNi_2O_4$. With increasing magnetic field, both T_{N1} and T_{N2} move to lower temperatures and the peaks become broader and flatter. Figure 5(b) shows the magnetic field dependences of T_{N1} and T_{N2} for $GeNi_{1.6}Co_{0.4}O_4$, where T_{N2} decreases more quickly than T_{N1} for this species. Variations of T_{N1}, T_{N2} and T_N with x in $GeNi_{2-x}Co_xO_4$ are shown in figure 6.

4. Discussion

Recently, the muon-spin relaxation study of $GeNi_2O_4$ reported by Lancaster *et al* [8] has shown evidence for phase separation into long-range-and short-range-ordered regions at low temperatures, and the short-range order is seen to persist across both transitions. In addition, the high magnetic field measurements show that, with $H = 14$ T, the transition temperatures only slightly decrease by about 0.5 K compared to the zero-field case, which explains the weak temperature dependence of T_{N1} and T_{N2} reported here with $H = 4.5$ T (figure 3). The

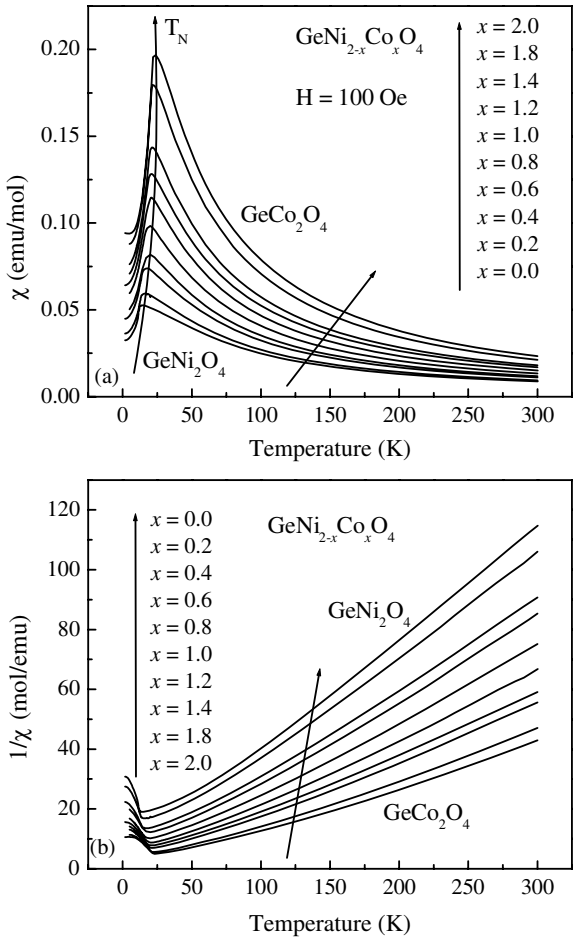

Figure 2. Temperature dependences of molar magnetic susceptibility χ (a) and its inverse $1/\chi$ (b) for $GeNi_{2-x}Co_xO_4$ with $H = 100$ Oe.

complicated evolution with magnetic field of the cusp at T_3 on the $d\chi/dT \sim T$ curve in this paper indicates a possible third magnetic transition in $GeNi_2O_4$. Previous specific heat measurements on polycrystalline pellets and single crystals [7, 9] both show a small cusp at around 11 K, but there is no comment on the nature of this phase transition in the literature.

Following the Goodenough–Kanamori rules [13], the exchange of Co–Co due to the overlap of the partially filled t_{2g} levels of Co^{2+} is ferromagnetic, and it is also ferromagnetic for the 90° Co–O–Co superexchange interaction. These interactions lead to the positive Weiss constant of $GeCo_2O_4$, $\theta = 40$ K. In order to explain the overall antiferromagnetic behaviour for $GeCo_2O_4$, the antiferromagnetic next-nearest-neighbour Co-superexchange interactions have to be included [14]. For $GeNi_2O_4$, the same direct exchange between Ni^{2+} ions is not allowed due to the filled t_{2g} levels. The antiferromagnetic interactions for Co^{2+} are stronger than those for Ni^{2+}, which leads to a high antiferromagnetic transition temperature. It then follows that the substitution of Co^{2+} for Ni^{2+} will have two effects: (i) an increase in the lattice parameter for small changes (which will only have a negligible effect on the orbital overlap); (ii) an enhancement of exchange interactions due to the depletion of the t_{2g} orbitals, which leads to the

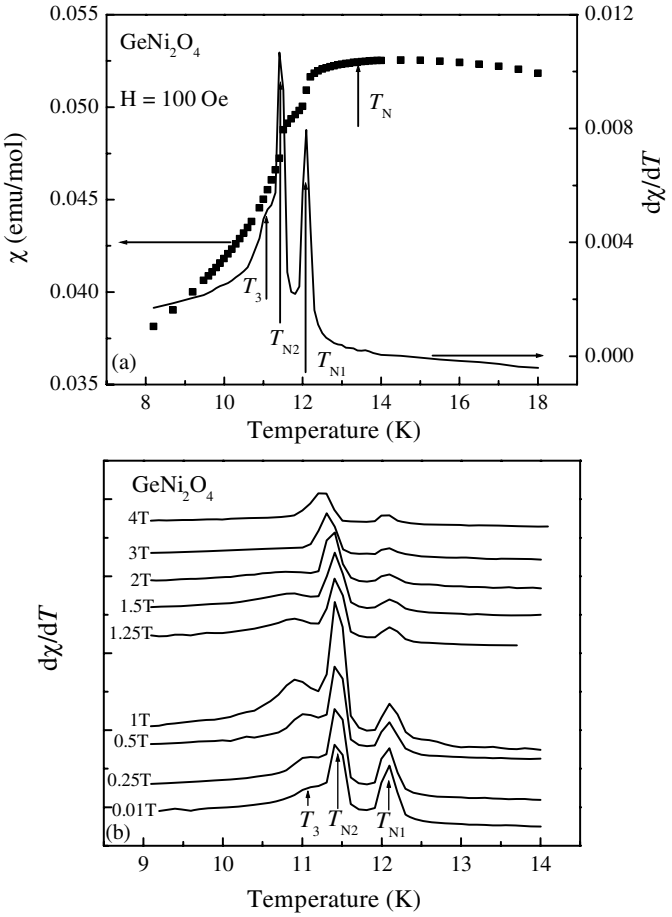

Figure 3. (a) Temperature dependences of molar magnetic susceptibility χ (solid circles) and its differentiation $\mathrm{d}\chi/\mathrm{d}T$ (solid line) for $GeNi_2O_4$ at low temperature with $H = 100$ Oe; (b) $\mathrm{d}\chi/\mathrm{d}T \sim T$ curves at different magnetic fields for $GeNi_2O_4$.

overall effect of higher transition temperatures. It is clear from the data that, with $x > 0.6$, the content of Co^{2+} overcomes a threshold value to build strong long-range magnetic ordering at low temperature and also suppresses the short-range magnetic ordering of Ni^{2+} spins near T_{N1}. The value of 0.6 is close to the percolation limit of the corner-shared tetrahedra sublattice (the pyrochlore lattice), which is $p_C = 0.39$, or $x = 0.8$ [15]. This is the doping limit at which, for random substitutions, long-range order is destroyed due to the destruction of nearest-neighbour links.

A natural question to ask is why does doping with a magnetic Ni^{2+} ion induce a change in behaviour at the percolation limit? This is also seen in the evolution of the Weiss temperature, in which a change in slope occurs above $x = 0.6$ (see figure 7). θ is small and negative for $GeNi_2O_4$, which is consistent with the other reported data [7]. For all Co doping samples, θ is positive. With increasing x, θ increases linearly, but there is a slope change beyond $x = 0.6$.

One explanation for this behaviour is that the Ni^{2+} ion acts like a non-magnetic impurity since Ni^{2+} has filled t_{2g} orbitals, whereas Co^{2+} has one unfilled t_{2g} orbital (in the high-spin state). The e_g orbitals are identical for both species; that is, they are both singly occupied; see

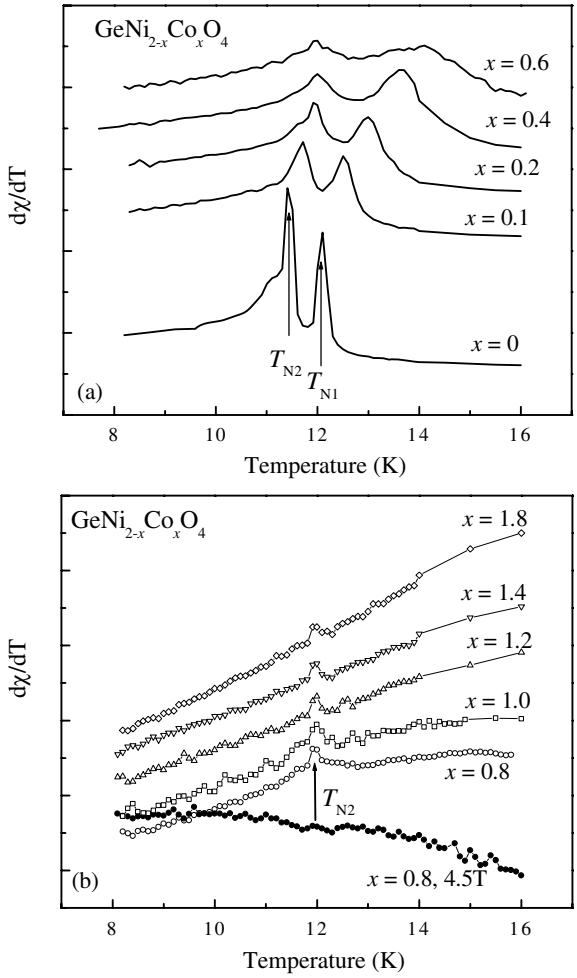

Figure 4. $d\chi/dT \sim T$ curves for $GeNi_{2-x}Co_xO_4$ with $x \leqslant 0.6$ (a) and $x > 0.6$ (b). All curves were measured with $H = 100$ Oe.

the inset of figure 7. The superexchange for Ni and Co is very different. Co has strong FM exchange due to the one empty electron in the t_{2g} orbital. Ni has weaker AF exchange due to the filled shell (there is only weak exchange with the e_g orbitals—the t_{2g} orbitals are filled). Next-nearest-neighbour AF exchange plays a very important role in this system. This is why the θ is negative in Co despite nearest-neighbour ferromagnetic exchange. It is also clear that the FM exchange is the reason for the dramatic differences between the two species $GeNi_2O_4$ and $GeCo_2O_4$. In the doping studies, there is no FM exchange allowed for the Co–O–Ni pathway because there is no electron to pair up with on the Ni site (it is in another orbital of different symmetry). Therefore, doping with Ni acts like an impurity—it disrupts the net change path. Once this gets down to the percolation limit of the lattice, one is left with only weaker AF interactions, which give rise to the complicated Ni behaviour. Even though Ni^{2+} is magnetic, the effect of doping for Co^{2+} results in the removal of these exchange pathways, and results in a lowering of θ. Percolation theory applied to the pyrochlore lattice works for this reason. Since the lattice parameter varies smoothly across the series (and the total change in lattice constant is

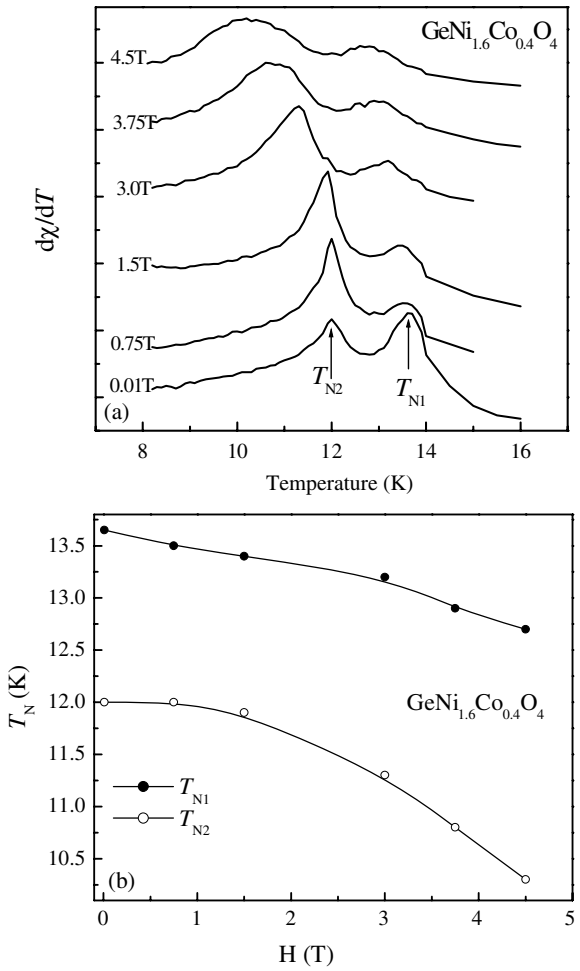

Figure 5. (a) $d\chi/dT \sim T$ curves at different magnetic fields for $GeNi_{1.6}Co_{0.4}O_4$; (b) variations of T_{N1} and T_{N2} with magnetic fields for $GeNi_{1.6}Co_{0.4}O_4$.

very small), the change in orbital overlap due to the expansion of the lattice with doping cannot explain the dramatic change beyond the $x = 0.6$ substitution.

Recent mean-field calculations have demonstrated the importance of next-nearest-neighbour interactions in stabilizing the antiferromagnetic structure in $GeCo_2O_4$ [11]. J_1 (near-neighbour interactions) is predicted to be ferromagnetic (which explains the positive Weiss temperature), but J_2 and J_3 are negative (which is why the structure is antiferromagnetic at low temperatures). The replacement of Co^{2+} with Ni^{2+} spins results in a systematic reduction of the Weiss temperature, which is naturally explained by the removal of nearest-neighbour exchange pathways. It is curious that $GeNi_2O_4$ has a change in sign of the Weiss temperature at only $x = 0.1$, or 5% doping with Co^{2+}. This suggests a very fragile ordered state for $GeNi_2O_4$. Inducing a small amount of t_{2g} overlap, through Co^{2+} substitution, drives the Weiss temperature to a net ferromagnetic rather than an antiferromagnetic interaction.

The magnetization measurements of $GeNi_{1.6}Co_{0.4}O_4$ provide more evidence for the phase separation of the system into short-ranged and long-ranged magnetically ordered states, as

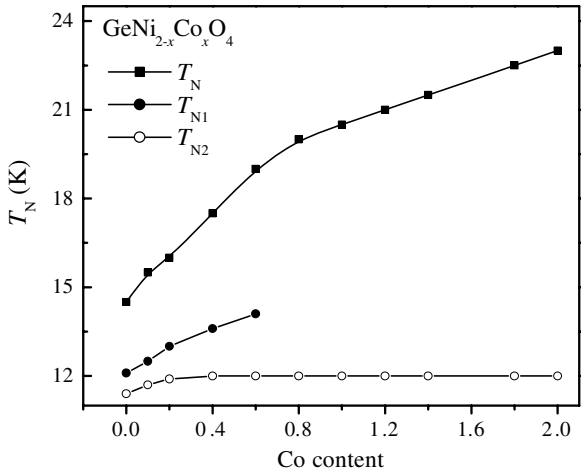

Figure 6. Variations of T_{N1}, T_{N2}, T_N with x for $GeNi_{2-x}Co_xO_4$. The data is obtained from the susceptibility measured with $H = 100$ Oe.

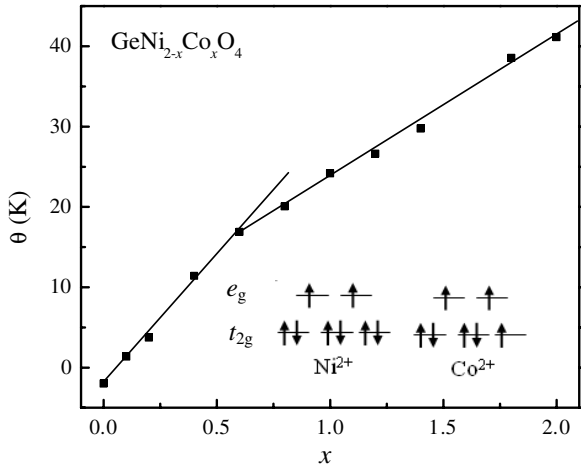

Figure 7. Variation of Curie–Weiss constant θ with x for $GeNi_{2-x}Co_xO_4$. The data is calculated from the susceptibility measured with $H = 100$ Oe. Inset: splitting of orbital levels for Ni^{2+} and Co^{2+} (high spin).

suggested by recent μSR experiments [8]. Previous magnetization measurements on pure $GeNi_2O_4$ do not show clear phase separation due to the small changes in T_{N1} and T_{N2}, even in applied fields up to $H = 14$ T. But for the $GeNi_{1.6}Co_{0.4}O_4$ sample, with increasing applied magnetic fields, both T_{N1} and T_{N2} clearly decrease, which shows the suppression of magnetic ordering under magnetic fields. Also, with increasing magnetic field, the peaks on $d\chi/dT \sim T$ curve become broad and flatten, which also supports this theory. For $H = 4.5$ T, the peak on T_{N1} almost disappears. These kinds of behaviour are all typical of a phase-separated system. The steep drop in T_{N2} with increasing magnetic field indicates that the long-range magnetic ordering is affected more strongly by an applied magnetic field than that for short-range magnetic ordering.

5. Conclusions

Solid-state solutions of the series $GeNi_{2-x}Co_xO_4$ have been prepared and studied through dc susceptibility measurements. Doping with the Ni^{2+} ion acts like a non-magnetic impurity due to the filling of the t_{2g} orbital, and a dramatic change in behaviour is noted near the percolation limit for the corner-shared tetrahedra lattice. A third phase transition at 11 K has been noted in the $GeNi_2O_4$ species which has only a weak magnetic field dependence. Evidence for phase separation into short-ranged- and long-ranged-ordered states is noted for all dopings less than $x = 0.6$ in the series and supports recent μSR work.

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