

## Impurity effects on the Ni<sup>3+</sup> triangular lattice of Ag<sub>2</sub>NiO<sub>2</sub>

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 145235

(<http://iopscience.iop.org/0953-8984/19/14/145235>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 17:29

Please note that [terms and conditions apply](#).

# Impurity effects on the Ni<sup>3+</sup> triangular lattice of Ag<sub>2</sub>NiO<sub>2</sub>

H Yoshida, Y Muraoka and Z Hiroi

Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

E-mail: [hyoshida@issp.u-tokyo.ac.jp](mailto:hyoshida@issp.u-tokyo.ac.jp)

Received 1 September 2006

Published 23 March 2007

Online at [stacks.iop.org/JPhysCM/19/145235](http://stacks.iop.org/JPhysCM/19/145235)

## Abstract

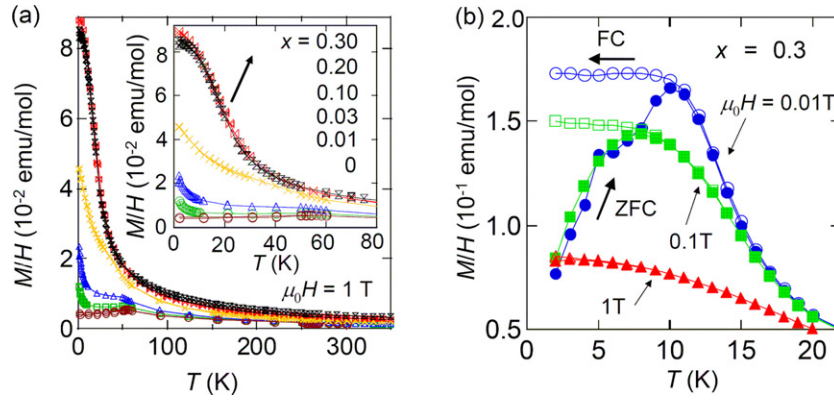
Silver oxonickelate Ag<sub>2</sub>NiO<sub>2</sub> is a metallic compound presenting a spin-1/2 triangular lattice. It exhibits a structural transition at  $T_s = 260$  K, which may be related to e<sub>g</sub> orbital ordering, and an antiferromagnetic transition at  $T_N = 55$  K. Impurity effects on its magnetic and electronic properties are examined by substituting Fe for Ni in Ag<sub>2</sub>Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>2</sub> ( $0 \leq x \leq 0.3$ ). A Curie-like enhancement in magnetic susceptibility is observed at low temperature, which implies that most Fe<sup>3+</sup> spins behave as free spins. Moreover, a large enhancement of residual resistivity and its suppression under magnetic fields are observed. Magnetic interactions in the Ni<sup>3+</sup> triangular lattice are discussed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Quantum phenomena on the triangular lattice have attracted many researchers, because associated geometrical frustration may suppress classical long-range order (LRO). It sometimes leads to a 'liquid' ground state with finite entropy [1]. There have also been extensive studies of the relation between orbital order and magnetic order on the triangular lattice, which has been explored in compounds such as LiNiO<sub>2</sub> [2, 3], NaNiO<sub>2</sub> [4, 5] and LiVO<sub>2</sub> [6].

Another Ni<sup>3+</sup> triangular lattice compound Ag<sub>2</sub>NiO<sub>2</sub> was found in 2002 by Schreyer *et al* [7]. The crystal structure is characterized by alternating stacking of a NiO<sub>2</sub> slab and a pair of staggered hexagonal silver layers. Since the formal valence distribution is (Ag<sub>2</sub>)<sup>+</sup> and Ni<sup>3+</sup>, the silver layers give rise to metallic conductivity coming from the quarter-filled Ag 5s band, while the NiO<sub>2</sub> layer presents a spin-1/2 triangular lattice with twofold spin and twofold orbital degeneracy, as evidenced by resistivity and magnetic susceptibility measurements [7–9]. Thus, Ag<sub>2</sub>NiO<sub>2</sub> is considered to be a unique system in which one expects an interesting interplay between conduction electrons and localized quantum spins on the frustrated lattice. It was reported that Ag<sub>2</sub>NiO<sub>2</sub> shows a structural phase transition at  $T_s = 260$  K, which may be related to orbital ordering, and an antiferromagnetic (AFM) transition at  $T_N = 55$  K [7–9]. We have



**Figure 1.** (a) Temperature dependence of magnetic susceptibility of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  ( $x = 0, 0.01, 0.03, 0.1, 0.2, 0.3$ ). (b) Spin glass like behaviour observed for  $x = 0.3$ .

discussed the relation between orbital order patterns and magnetic interactions in the  $\text{NiO}_2$  plane from the viewpoint of superexchange interactions, and suggested that AFM interactions dominate in the  $\text{NiO}_2$  plane [9]. Recent  $\mu\text{SR}$  experiments showed that incommensurate AFM order takes place in the  $\text{NiO}_2$  plane below  $T_N$  [10].

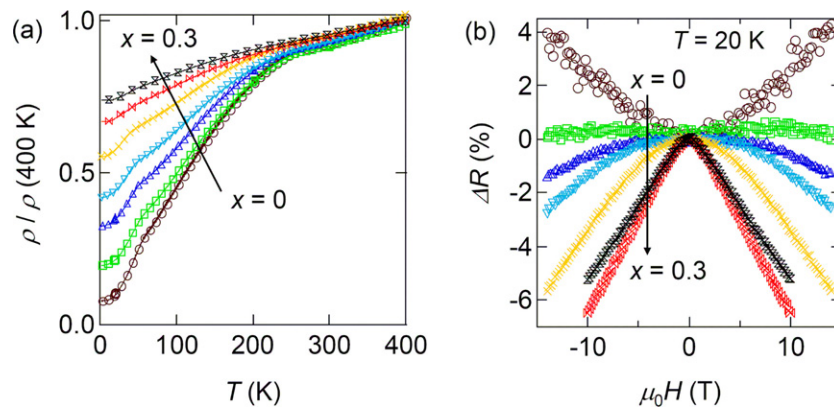
Here, we study impurity effects on the orbital and magnetic orders of  $\text{Ag}_2\text{NiO}_2$ . An  $\text{Fe}^{3+}$  ion, which has a  $3d^5$  state with  $S = 5/2$ , is substituted for a  $\text{Ni}^{3+}$  ion with  $S = 1/2$  in the chemical formula  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$ . Changes in magnetic susceptibility and resistivity with Fe substitution are investigated. It is shown that the results are consistently interpreted by the orbital order and magnetic interactions proposed in our previous paper [9].

## 2. Experimental details

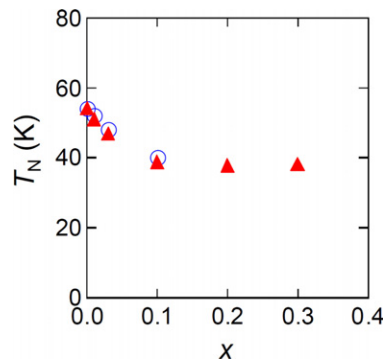
A series of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  powder samples was prepared by the solid-state reaction of  $\text{Ag}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{NiO}$  under high oxygen pressure, as reported previously [7, 9]. A single-phase sample was obtained for  $x \leq 0.3$ , as examined by powder x-ray diffraction measurements. For  $x = 0.5$ , a small amount of  $\text{AgFeO}_2$  was detected as an impurity phase. It is reasonable to assume that the  $\text{Fe}^{3+}$  ion replaces a  $\text{Ni}^{3+}$  ion, because a trivalent state is likely most stable for Fe for these preparation conditions. Magnetic susceptibility measurements were performed in the temperature range 2–350 K in a Quantum Design magnetic property measurements system (MPMS). Resistivity measurements were carried out in the temperature range 2–400 K on a compressed pellet by the standard four-probe method in a Quantum Design physical property measurements system (PPMS). Magnetoresistance measurements were also carried out in the PPMS under magnetic fields up to 14 T at 20 K.

## 3. Results and discussion

Figure 1(a) shows the temperature dependence of magnetic susceptibility of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  ( $0 \leq x \leq 0.3$ ). A large Curie-like enhancement is observed at low temperature with increasing Fe content up to  $x = 0.1$ . This enhancement may be due to free  $\text{Fe}^{3+}$  spins. Assuming  $S = 5/2$ , the amount of free spins is estimated to be 0.016 and 0.034 Fe/formula unit based on the Curie law for samples with  $x = 0.01$  and 0.03, respectively. Therefore, it is concluded that most of the substituted  $\text{Fe}^{3+}$  spins behave as free spins in the matrix of ordered  $\text{Ni}^{3+}$  spins.



**Figure 2.** Temperature dependence of resistivity of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  ( $x = 0, 0.01, 0.03, 0.05, 0.1, 0.2, 0.3$ ) (a), and the  $x$  dependence of magnetoresistance measured at 20 K (b).



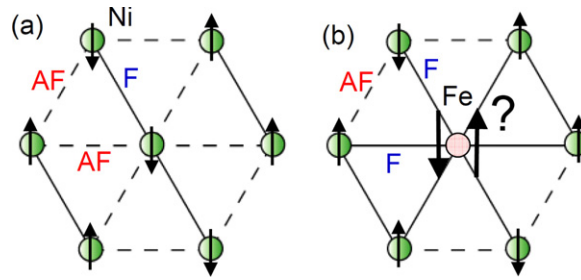
**Figure 3.**  $x$  dependence of  $T_N$  determined from resistivity (triangle) and magnetic susceptibility (circle) measurements.

This suggests that magnetic interactions between  $\text{Fe}^{3+}$  and  $\text{Ni}^{3+}$  spins are effectively cancelled due to certain frustration.

On the other hand, spin glass behaviour was observed for larger Fe substitution,  $x \geq 0.2$ . As shown in figure 1(a), the increase of susceptibility at low temperature seems to saturate for  $x = 0.2$  and  $0.3$ . The field dependence is shown in figure 2(b) for  $x = 0.3$ , where spin glass like behaviour is clearly seen: at low magnetic field, a large thermal hysteresis is detected between a heating curve after zero-field cooling and a cooling curve in a field. This fact implies that at high concentration Fe spins are not free but may form a small magnetic cluster.

The temperature dependence of resistivity for the solid solution is shown in figure 2(a). All samples investigated show metallic resistivity. The anomaly at  $T_N$  shifts to a lower temperature with increasing  $x$ . The  $x$  dependence of  $T_N$  is shown in figure 3.  $T_N$  decreases rapidly until  $x = 0.1$ , and becomes independent of  $x$  at around 40 K. The fact that  $T_N$  is not affected much at such high Fe concentration means that the introduction of  $\text{Fe}^{3+}$  spins does not destroy the LRO of  $\text{Ni}^{3+}$  spins, so  $\text{Fe}^{3+}$  spins coexist as free spins or clusters.

The most interesting finding on the impurity effect is the large enhancement of residual resistivity, as shown in figure 2(a). The residual resistivity ratio  $RRR$  is approximately 10 for  $x = 0$ , and it is reduced to 1.3 for  $x = 0.3$ . Such a large enhancement of residual resistivity



**Figure 4.** Possible spin arrangement of  $\text{Ag}_2\text{NiO}_2$  expected from an orbital order pattern (a) and the effect of Fe substitution (b).

is attributed to the reduction of the mean free path of carriers due to impurity scattering. In the present case, we expect a large magnetic scattering of conducting carriers in the  $\text{Ag}_2$  layers due to free  $\text{Fe}^{3+}$  spins in the  $\text{NiO}_2$  plane.

We also investigated the magnetic field dependence of resistivity, as shown in figure 2(b) for  $T = 20$  K. The magnetoresistance is slightly positive for a pure sample, while it becomes negative for substituted samples. The magnitude of the negative magnetoresistance increases rapidly with increasing  $x$ . For example, it is  $-5.6\%$  at  $H = 14$  T for  $x = 0.1$ . Interestingly, the field dependence is quadratic for small  $x$ , but tends to be linear for larger  $x$ . This negative magnetoresistance is attributed to the suppression of the magnetic scattering due to free Fe spins by applying a magnetic field.

$\text{Ag}_2\text{NiO}_2$  exhibits a second-order structural phase transition at  $T_s$ . We have proposed a possible orbital ordering model assuming a ferro-orbital order of  $d_{x^2-y^2}$  type [8, 9].  $T_s$  can be determined from the kinks observed in the temperature dependences of magnetic susceptibility and resistivity. It seems that  $T_s$  decreases slightly with increasing  $x$ , though the kinks become obscure as  $x$  increases. Since an  $\text{Fe}^{3+}$  ion lacks orbital degeneracy, a dilution of the  $d_{x^2-y^2}$  orbital order may occur with the substitution, which causes the reduction of  $T_s$  and the suppression of orbital order.

A possible spin arrangement in the Ni plane is depicted in figure 4. It was deduced from considerations on the magnetic couplings based on the orbital order model. In this model, two sides of a  $\text{Ni}^{3+}$  triangle have an AFM interaction and one side has an FM interaction as a result of the  $d_{x^2-y^2}$  orbital ordering. The expected spin arrangement below  $T_N$  is illustrated in figure 4(a). Here, we discuss the spin state of a substituted  $\text{Fe}^{3+}$  ion based on this model in order to explain the observed magnetic and electrical properties of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$ . Since an  $\text{Fe}^{3+}$  ion has five 3d electrons in the high-spin state, there is no orbital degeneracy. According to the Goodenough rule modified by Kanamori, the superexchange interaction between Fe and Ni is expected to be FM, because the Fe–O–Ni bond angle is nearly  $90^\circ$  [11]. Then, interactions between an Fe spin in the centre and the surrounding six Ni spins are frustrated, as shown in figure 4(b): four of them with up spins try to force the Fe spin up, while the rest with down spins must act inversely. Due to this frustration, an Fe spin tends to be decoupled from Ni spins in the matrix and behave as an almost free spin at low temperature. However, this simple model considering only nearest-neighbour interactions may not be enough. In fact, recent  $\mu\text{SR}$  experiments indicate that there exists incommensurate AFM order in the  $\text{NiO}_2$  plane. To clarify these issues, neutron diffraction experiments on pure and Fe-doped samples are in progress.

On the other hand, the situation may be modified for higher Fe concentration. Then another  $\text{Fe}^{3+}$  ion might replace one of the six adjacent Ni ions, the probability of which increases with  $x$ . A simple estimation of a critical concentration  $x_c$  is  $1/6 \sim 0.16$ . In such an Fe pair

or a cluster,  $\text{Fe}^{3+}$  spins should be coupled to each other ferromagnetically. Therefore, one expects an FM cluster that is embedded in a matrix made of  $\text{Ni}^{3+}$  spins, resulting in spin glass behaviour at high Fe concentration. In fact, the change from free spin to spin glass behaviour is observed for Fe concentration between 0.1 and 0.2, just around  $x_c = 0.16$ . In terms of site percolation on the triangular lattice, it is known that the critical concentration at which  $\text{Fe}^{3+}$  ions form a path from one end to the other end of a sample is 50%. FM LRO would set in at such a high Fe concentration, but it is beyond the solubility limit in the present compound. The spin glass behaviour in the present system is similar to those in conventional spin glass systems such as  $\text{Au}_{1-x}\text{Fe}_x$ , where cluster spin glass behaviour appears at Fe concentration  $0.01 \leq x \leq 0.15$  [12, 13]. It is interesting to note that the  $\text{NiO}_2$  plane of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  behaves as a non-magnetic medium due to inherent coexistence of FM and AFM interactions on the triangular lattice.

#### 4. Conclusion

We have studied the electrical and magnetic properties of  $\text{Ag}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_2$  ( $0 \leq x \leq 0.3$ ). It is found that both the magnetic and orbital order are rather insensitive to Fe substitution. Most of the  $\text{Fe}^{3+}$  spins behave as free spins for  $x \leq 0.1$ , while cluster spin glass behaviour is observed for  $x \geq 0.2$ . These results are qualitatively explained based on a model previously proposed for the spin-1/2 triangular lattice with ferro-orbital order in  $\text{Ag}_2\text{NiO}_2$ .

#### Acknowledgments

We are grateful to T Sörgel and M Jansen for helpful discussions. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas (Invention of Anomalous Quantum Materials) provided by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

#### References

- [1] Anderson P W 1973 *Mater. Res. Bull.* **8** 153
- [2] Hirakawa K, Kadowaki H and Ubukoshi K 1985 *J. Phys. Soc. Japan* **54** 3526
- [3] Yamaura K, Takano M, Hirano A and Kanno R 1996 *J. Solid State Chem.* **127** 109
- [4] Chappel E, Nunez-Regueiro M D, Dupont F, Chouteau G, Darie C and Sulpice A 2000 *Eur. Phys. J. B* **17** 609
- [5] Chappel E, Nunez-Regueiro M D, Chouteau G, Isnard O and Darie C 2000 *Eur. Phys. J. B* **17** 615
- [6] Pen H F, van den Brink J, Khomskii D I and Sawatzky G A 1997 *Phys. Rev. Lett.* **78** 1323
- [7] Schreyer M and Jansen M 2002 *Angew. Chem.* **41** 643
- [8] Yoshida H, Muraoka Y, Hiroi Z, Sörgel T and Jansen M 2005 *AIP Conf. Proc. 24th Int. Conf. on Low Temperature Physics* at press
- [9] Yoshida H, Muraoka Y, Sörgel T, Jansen M and Hiroi Z 2006 *Phys. Rev. B* **73** 020408(R)
- [10] Sugiyama J, Ikedo Y, Mukai K, Brewer J H, Ansaldò E J, Morris G D, Chow K H, Yoshida H and Hiroi Z 2006 *Phys. Rev. B* **73** 224437
- [11] Kanamori J 1959 *J. Phys. Chem. Solids* **10** 87
- [12] Coles B P, Sarkissian B V B and Tayler R H 1978 *Phil. Mag.* **37** 489
- [13] Murani A 1978 *J. Appl. Phys.* **49** 1604