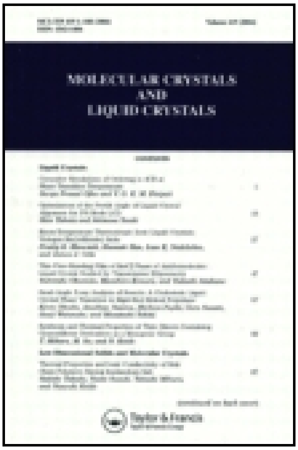

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Magnetic Structure of $Li_{1-x}Ni_{1+x}O_2$

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(In final form June 28, 1999)

To describe the magnetic properties of the layered $Li_{1-x}Ni_{1+x}O_2$ compounds we use a mean field model with a weak ferromagnetic coupling J_F^2 within the Ni planes between Ni^{3+} ions, an interlayer antiferromagnetic interaction J_{AF} between Ni^{2+} present in the Li layers and their Ni^{3+} nearest neighbours and an intraplane ferromagnetic interaction J_F^1 between Ni^{2+} and Ni^{3+} ions in the Ni planes. The hierarchy $|J_F^1| > |J_{AF}| > |J_F^2|$ is deduced from experimental data.

Keywords: layered compounds; magnetic clusters

INTRODUCTION

The $Li_{1-x}Ni_{1+x}O_2$ system has been considered as a possible quantum spin liquid[1], a 2D frustrated antiferromagnet[2], a weakly coupled 2D Ising ferromagnet[3], a 2D Heisenberg ferromagnet[4], a spin glass[5,6], as ferromagnetic (F) clusters within a frustrated antiferromagnetic (AF) matrix[7], an inhomogeneous magnet[12], a quantum spin-orbital liquid[8,9]. Some of these interpretations are consequences of not well characterized compounds, as magnetic properties of $Li_{1-x}Ni_{1+x}O_2$ are extremely sensitive to the preparation conditions.

Here, based on a systematic experimental study performed on carefully characterized samples[10], a new theoretical scheme is proposed based on the formation of: ferromagnetic clusters.

Structure study[7] shows that, for x < 0.24, extra Ni atoms are always present in the Li planes, leading to the effective formula, $\left[Li^{+}_{1-x}Ni^{2+}_{x}\right]_{L}\left[Ni^{2+}_{x}Ni^{3+}_{1-x}\right]_{H}O_2$.

SIGN OF THE MAGNETIC INTERACTIONS

In the NiO_2 slabs there are only nearly 90° $Ni-O-Ni$ bonds, while the presence of Ni^{2+} ions in the Li planes introduces 180° $Ni-O-Ni$ bonds. Thus, according to the Goodenough-Kanamori-Anderson (GKA) rules[11], i) each Ni^{2+} ion in a Li layer couples ferromagnetically its nearest neighbors (n.n.) in the two adjacent Ni planes (3x2=6 ions), independent of the sign of the $Ni^{3+}-O-Ni^{2+}$ interlayer interaction. However, the 180° angle between the Ni^{3+} and the Ni^{2+} ions connected through the oxygen favors an AF coupling. Since virtual excitations involve the same $O2p$ orbital, the s=1/2 *and s=1 spins of those ions must be antiparallel. ii) in the* Ni^{3+} planes, where the Ni^{3+} ions are connected *via* the oxygen with 90° bond, we cannot derive a conclusion from GKA rules because in this geometry two $O2p$ orbitals are involved, the coupling will be weaker but can have, in principle, both signs, F or AF. However, Hund's rule acting on the oxygen atom will favor an F interaction. The intralayer coupling between Ni sites is F and therefore, there is no geometrical frustration in the Ni planes. Also in $NaNiO_2$, the intraplane interactions are F. In this stoichiometric compound the interaction between n.n. Ni^{3+} planes although weak, is AF, giving rise to a 3D A-type antiferromagnet. In the $Li_{1-x}Ni_{1+x}O_2$ compounds the distance between n.n. Ni^{3+} planes is even shorter but this AF interaction is overcome by the stronger F interaction induced by the excess Ni^{2+} ions in the Li planes. This indirect frustration effect and the high value of the cluster magnetization could explain why no long range F order of the planes has been observed.

In order to achieve electroneutrality xNi^{2+} ions are in the Ni^{3+} planes. Let J_F^1 be the F interaction between them and their n.n. Ni^{3+}.

CLUSTER MODEL

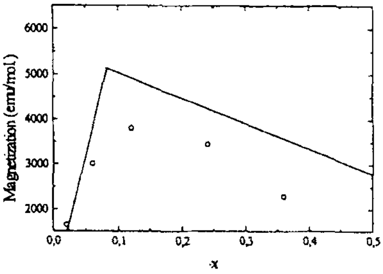

FIGURE 1 saturation magnetization of the $Li_{1-x}Ni_{1+x}O_2$ family, straight lines: equations given in the text, open dots: experimental data in an 11 T field.

Each Ni^{2+} ion in the Li plane connects ferromagnetically 6 Ni ions in the Ni planes: 3 on each adjacent Ni layer. Then for $x = 1/6$ homogeneously distributed Ni^{2+} ions all sites are coupled. In addition, each Ni^{2+} ion in the Ni plane has a strong J_F^1 interaction with its 6 n.n. Ni^{3+} in the same plane, this number is thus reduced to $x = 1/12$. Therefore, at low concentration, ($x < x_c$), the magnetization M_c increases, due to the formation of these F clusters. For $x > x_c$ a decrease of M_c due to the AF correlations between the excess $Ni^{2+} - O - Ni^{3+}$ bonds from Li and Ni planes respectively, is predicted. With M and M' the magnetic moment of the Ni^{3+} ions and the induced magnetic moment on Ni^{3+} ions by the Ni^{2+} ions in the Ni layers, respectively, one has, $M_C = 5xM + 6xM'$ for $x < x_c$ and $M_C = \frac{11}{12}M - (x - \frac{1}{12})M'$ for $x > x_c$. In Figure 1, straight lines represent these formulae. Good qualitative agreement is found with experiment, (open dots), up to x = 0.24 beyond which a change in the chemical structure occurs, (*Li* ions going into the *Ni* slabs). Calculations have been performed in the non physical $\chi < o$ region just to show more clearly the intercept with the temperature axis.

HIERARCHY OF THE MAGNETIC INTERACTIONS

We write the molar magnetization, using the effective chemical formula given above, in the diluted limit (i.e. without interaction between clusters),

$M_T = (1-x)m_{Ni^{3+},H} + xm_{Ni^{2+},H} + xm_{Ni^{2+},L}$, with, $m_{Ni^{(i)},H_j} = c_i \frac{H_j}{T}$,

$c_i = \frac{N_A \mu_B^2}{3k_B} g_i^2 J_i(J_i+1)$, where $j = H$ *or* L for the magnetic ions, in the Ni and Li planes respectively. We find,

$$H_H = H_0 - \gamma x m_{Ni^{2+},L} + \alpha(1-x)m_{Ni^{3+},H}\,,\quad H_L = H_0 - \gamma x m_{Ni^{2+},L} - \gamma(1-x)m_{Ni^{3+},H}$$

$$\chi^{-1} = \frac{M_T}{H_0} \approx T \cdot \left[x + \frac{\frac{3}{8}(1+\frac{5}{3}x)(1-x\frac{\gamma}{T})^2}{1-\frac{3}{8T}(\alpha x(1-x)+x\frac{\gamma^2}{T}(1+\frac{5}{3}x))} \right]^{-1} \qquad (1)$$

in mol./emu units, with, $\gamma = -(11-5x)J_{AF}$, and, $\alpha = \frac{2}{1+x}[11xJ_F^1 + 8(1-x)J_F^2]$, In the high temperature paramagnetic limit Eq.(1) leads to, $S = \frac{d}{dT}(\chi^{-1}) = 8/(3+13x)$ which only depends on x, while the position of the straight line in the $\chi^{-1} vs. T$ plot is given by the interactions. Fitting Eq.(1) with the results for two samples ($x_1 = 0.08$ and $x_2 = 0.11$) we derive $J_{AF} = (-15 \pm 5)K$, $J_F^1 = (45 \pm 5)K$ and $J_F^2 = (8 \pm 3)K$. The calculated Curie temperatures ($T_C^1 = 40K$ and $T_C^2 = 60K$) are in good agreement with experiment. However, the values of x derived from S are higher than those determined from the Rietveld analysis ($x_1 = 0.03$ and $x_2 = 0.05$). This could be due to partial oxygen loss , which results in an increase of the Ni^{2+} concentration.

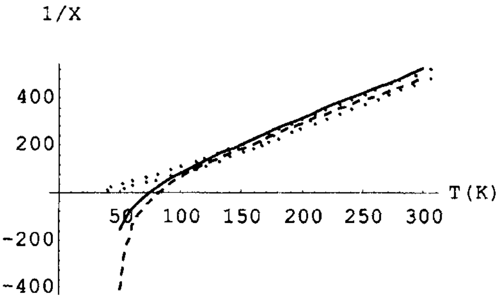

FIGURE 2. χ^{-1} of the two concentrations (see text). Dots: experiment[13]. Calculation: continuous line low concentration, dashed line stronger one.

DISCUSSION AND CONCLUSION

The intraplane interactions are ferromagnetic (J_F^1 and J_F^2), and there is no frustration in the triangular lattice, therefore $Li_{1-x}Ni_{1+x}O_2$ is not a quantum spin liquid[1]. The interplane interaction between Ni^{2+} ions in the Li planes and Ni^{3+} (or Ni^{2+}) ions in the heavy planes are AF in agreement with GKA rules and the measured $M_c vs. x$ dependence. However this J_{AF} interaction leads to an F coupling of adjacent Ni planes. The clusters formed in this way control the physics of this compound. This interplane J_{AF} interaction is significantly stronger than the one between adjacent Ni planes in the stoichiometric compound $NaNiO_2 (\approx 2K)$. The small value of J_F^2 is in agreement with GKA predictions. J_F^1 is much larger than J_F^2 as expected from the different numbers of electrons of connected *Ni* ions. Within error bars, we find $|J_F^1| > |J_{AF}| > |J_F^2|$.

We have recently performed magnetic measurements on a very pure compound ($x_{nominal} \approx .004$) showing striking analogies with $NaNiO_2$. This seems to rule out the interpretation attributing to orbital disorder [9] the absence of long range ferromagnetic order in $LiNiO_2$, because the isomorphic $NaNiO_2$ orders below ≈ 20 K.

References

[1] K. Hirakawa, H. Kadowaki, and K. Ubukoshi, *J. Phys. Soc. Jpn.*, **54,** 3526 (1985); K. Hirakawa, R. Osborn, A.T. Taylor, and H. Yasuoka, *J. Phys. Soc. Jpn.*, **59,** 3081 (1990).

[2] K. Hirota, Y. Nakazawa, and M. Ishikawa, *J. Magn. Magn. Mater.*, **90&91,** 279 (1990); H. Yoshizawa, H. Mori, K. Hirota, and M. Ishikawa, *J. Phys. Soc. Jpn.*, **59,** 2631 (1990); K. Hirota, H. Yoshizawa, and M. Ishikawa, *J. Phys.: Condens. Matter.*, **4,** 6291 (1992).

[3] J.P. Kemp, P.A. Cox and J. Hodby, *J. Phys.: Condens. Matter.*, **2,** 6699 (1990).

[4] R. Stonayova, E. Zhecheva and C. Friebel, *J. Phys. Chem. Solids*, **54,** 9 (1993).

[5] J. N. Reimers et al., *Solid State Chem.*,. **102,** 542 (1993).

[6] A. Bajpai and A. Banerjee, *Phys. Rev. B*, **55,** 12439 (1997).

[7] A.Rougier, C. Delmas and G. Chouteau, *J. Phys. Chem. Solids*, **57,** 1101 (1996) ; ref. therein.

[8] L.F. Feiner, A.M. Oleš, and J. Zaanen, *Phys. Rev. Lett.*, **78,** 2799 (1997).

[9] Y. Kitaoka et al., *J. Phys. Soc. Jpn.*, **67,** 3703 (1998).

[10] A.- L. Barra, G. Chouteau, A. Stepanov, A. Rougier, and C. Delmas, *Europ. Phys. J. B*, **7,** 551 (1999).

[11] D.I. Khomskii and G.A. Sawatzky, *Solid State Comm.*, **102,** 87 (1997).

[12] C.B. Azzoni, A. Paleari, V. Massarotti, M. Bini, and D. Capsoni, *Phys. Rev. B*, **53,** 703 (1996).

[13] J. P. Peres, PhD Bordeaux, 1996, unpublished.