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## LETTER TO THE EDITOR

# Magnetic susceptibility studies of $\text{LiNiO}_2$ and $\text{NaNiO}_2$

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**Abstract.** The temperature variation of the magnetic susceptibility of the compounds  $\text{LiNiO}_2$  and  $\text{NaNiO}_2$  has been measured. Contrary to a previous report by Hirakawa and co-workers, which claimed that these materials were antiferromagnetically coupled, and so could potentially possess quantum liquid ground states, our data suggest that these materials behave as weakly coupled 2D Ising ferromagnets. We show that this conclusion is in fact supported by much of the data in the previous report.

It was first suggested by Anderson [1] that for a spin-half two-dimensional trigonal lattice antiferromagnet, it is possible to construct a quantum liquid ('resonating valence bond') ground state with no long range magnetic order, with lower energy than the classical Néel ground state. There has since been a substantial amount of research effort devoted to both theoretical studies of the ground state of this system [2, 3], and to the search for materials with the requisite structure and magnetic coupling [4, 5]. The theoretical studies in particular have acquired some impetus [6–8] following the suggestion that such an RVB ground state could be responsible for high- $T_c$  superconductivity in copper oxide systems [9].

Two compounds with potential to be  $S = \frac{1}{2}$  2D trigonal antiferromagnets are  $\text{NaNiO}_2$  and  $\text{LiNiO}_2$ . These are both based on a sodium chloride structure, but with the alkali metal (A) and transition metal (M) ordered onto alternate (111) planes. The structure may also be viewed as a layer structure, with trigonally packed layers of atoms in the order O–A–O–M– with ABC stacking. The distance between successive layers of M is of the order of 5 Å, compared with an M–M distance within the layers of 2.8–3 Å [10]. The magnetic behaviour should therefore be dominated by the intralayer interactions.

In the nickel compound, the formal oxidation state is  $\text{Ni}^{3+}$ , which is  $3d^7$ . The local environment around the transition metal ions is trigonally distorted octahedral, and for  $d^7$ , there may be both high-spin (from octahedral  ${}^4T_1$ ) and low-spin ( ${}^2E$ ) states, where the latter should be preferred on account of the high formal oxidation state of Ni giving rise to strong Ni–O interactions. ESR studies of  $\text{Ni}^{3+}$  impurities in oxides [11] show that this is in fact the case. There should also be a Jahn–Teller distortion to lift the twofold orbital degeneracy, but this should not greatly affect the magnetic moment, since there is no orbital contribution in an E state.

The Ni and Ti compounds were studied by Hirakawa *et al* by magnetic susceptibility and neutron scattering [4], and also by ESR [12]. The neutron measurements on both compounds showed no evidence of long range antiferromagnetic order, down to 1.3 K,

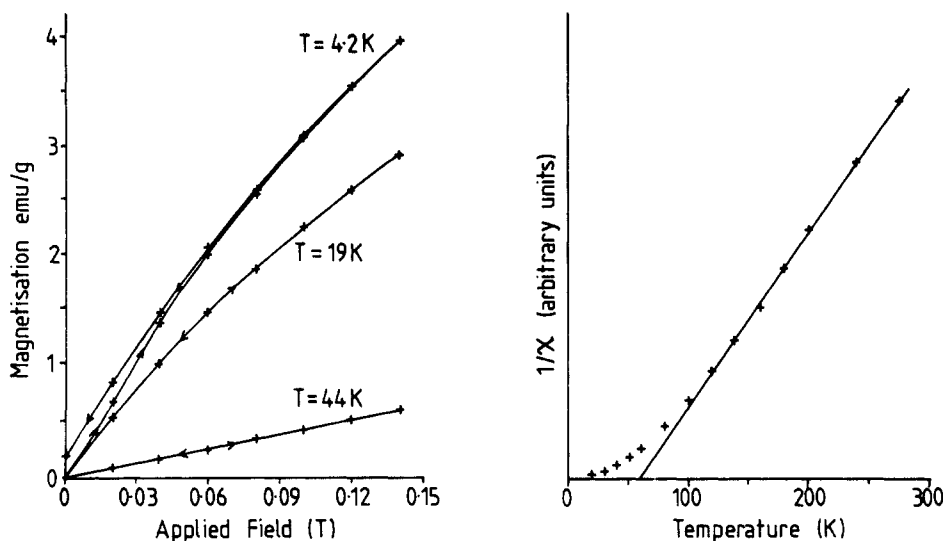
while the susceptibility measurements showed paramagnetic behaviour down to 4.2 K for  $\text{NaTiO}_2$  and were claimed to show ferrimagnetic ordering for  $\text{LiNiO}_2$  below 210 K. The ESR measurements on the latter showed strong anisotropy, suggesting that the in-plane magnetic interactions were Ising-like. The authors concluded that both materials were promising candidates for possessing a quantum liquid ground state.

Our work was motivated by the fact that it is possible to remove the alkali metal from these materials in a controlled fashion, by either chemical or electrochemical means [13–15], while still preserving the layer structure. This process results in oxidation of the transition metal ion, from  $S = \frac{1}{2}$  to  $S = 0$ , and thus the introduction of holes into the system. In the RVB theory of superconductivity, holes in an RVB ground state behave as bosons [9], and can undergo Bose–Einstein condensation to the superconducting state. We had therefore intended to extend the work in [4] by studying the magnetic properties of the phases  $\text{Li}_x\text{NiO}_2$  and the isostructural  $\text{Na}_x\text{NiO}_2$  for  $x \leq 1$ . However, in this letter, we present results demonstrating that these materials in fact show weak *ferromagnetic* coupling, and that the temperature variation of the susceptibility above the Curie temperature agrees closely with that predicted by a two-dimensional Ising model.

$\text{NaNiO}_2$  and  $\text{LiNiO}_2$  were synthesised by heating intimately ground mixtures of  $\text{Li}_2\text{CO}_3$  or  $\text{Na}_2\text{O}_2$  and  $\text{NiO}$  in alumina boats under pure dry oxygen for periods of up to 36 h, at temperatures of 800 °C (Li) or 700 °C (Na). At the end of the period the samples were allowed to cool slowly to room temperature, still under oxygen. Particular care must be taken with these syntheses, since the products are rather prone to non-stoichiometry, via alkali metal loss through evaporation or diffusion into the crucible. For  $\text{LiNiO}_2$  in particular, it is possible to isolate a continuous range of NaCl-type phases  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  for  $0 \leq x \leq 1$  [16], where the oxidation state of the Ni varies from +3 to +2. In this work two samples of  $\text{LiNiO}_2$  were studied. The first was made stoichiometric quantities of  $\text{Li}_2\text{CO}_3$  and  $\text{NiO}$ , fired in a new crucible. Powder diffraction showed this to be a single phase, but with *a*- and *c*-parameters slightly larger than those for  $\text{LiNiO}_2$ , which tends to be characteristic of Li deficiency [16]. Analysis for metals by atomic absorption showed an Li:Ni ratio of  $0.93 \pm 0.05$  and oxidation state analysis by monitoring the mass loss during reduction in hydrogen at 800 °C showed the mean oxidation state of Ni was 2.82. A second sample was made by firing a mixture with 3% excess  $\text{Li}_2\text{CO}_3$  in a pre-equilibrated crucible (one in which an  $\text{Li}_2\text{CO}_3/\text{NiO}$  mixture had previously been fired). Powder diffraction again showed this to be a single phase but with lattice parameters much closer to those for  $\text{LiNiO}_2$ . Atomic absorption gave the Li:Ni ratio as  $1.02 \pm 0.05$ , and hydrogen reduction gave the mean oxidation state of Ni as 3.02.

At high temperature,  $\text{NaNiO}_2$  is isostructural with the Li compound, but transforms below 495 K to a monoclinically distorted variant [17]. The powder diffraction pattern of our sample was a mixture of the two phases. The Na:Ni ratio from atomic absorption was  $1.05 \pm 0.05$ , and oxidation state analysis by iodometric titration showed that the mean oxidation state of Ni was 2.90.

Magnetic susceptibilities were measured using a vibrating sample magnetometer. Temperature control in this instrument was provided by an Oxford Instruments liquid helium-4 cryostat. It is unfortunately not possible to control the temperature of this below  $\approx 10$  K, but a steady temperature of 4.2 K may be achieved by isolating the cryostat heater, and allowing the lower part of the cryostat to flood with liquid helium. Magnetisation as a function of field was measured for a series of temperatures between 290 K and 4.2 K, the applied field being provided by a water-cooled solenoid which was swept between  $\pm 0.15$  T (1500 G). The samples were in the form of up to 100 mg of finely ground powders, packed into a screw-together nylon holder.



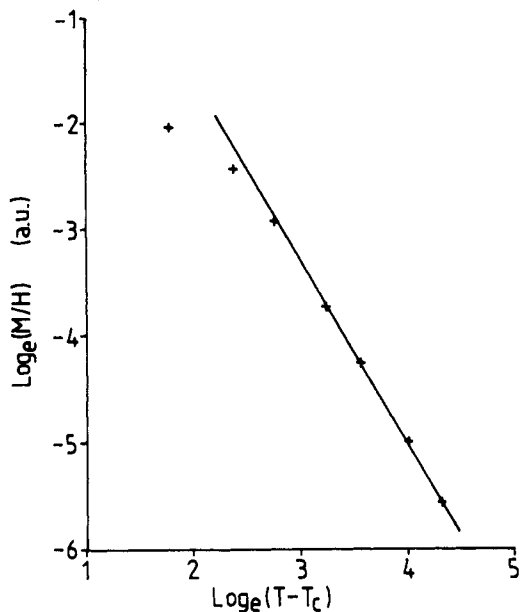
**Figure 1.** Left hand graph: magnetisation versus field for the most stoichiometric sample of  $\text{LiNiO}_2$  at three different temperatures. The arrows indicate the direction of field sweep. Right hand graph: Curie-Weiss plot of the susceptibility, using  $\chi = M/H$  at  $H = 0.14$  T. The behaviour is typically ferromagnetic.

Figure 1 shows some of the raw magnetisation versus field behaviour for the second (the most stoichiometric) sample of  $\text{LiNiO}_2$ . At high temperatures (above about 30 K),  $M$  was linear in  $H$  for fields of up to 0.15 T. Below this temperature, some non-linearity became evident, as in this temperature range the magnetisation was becoming large, and was presumably nearing saturation. Down to 10 K, no spontaneous magnetisation at zero field was observed, and the magnetisation was independent of the direction in which the field was swept. At 4.2 K, however, figure 1 shows that hysteresis in  $M$  versus  $H$  is observable, characteristic of a ferromagnet below its Curie temperature. This pattern of behaviour was also observed for the first sample of  $\text{LiNiO}_2$  (the less stoichiometric one) and also for  $\text{NaNiO}_2$ . Thus all three compounds appear to be ferromagnetic, with a Curie temperature in the range 4.2–10 K. This would immediately explain why no magnetic peaks are seen in the neutron scattering pattern of  $\text{LiNiO}_2$  [1], since for a ferromagnet the magnetic and crystal lattices coincide.

The right-hand portion of figure 1 shows a Curie-Weiss ( $1/\chi$  versus  $T$ ) plot for the second  $\text{LiNiO}_2$  sample, with the susceptibility evaluated from  $M/H$  at 0.14 T. This has an intercept of  $\theta = 60$  K, again indicating that the coupling in the system is ferromagnetic, although rather weak. In mean field theory, the slope of this line should be the same as for a purely paramagnetic system with the same magnetic moment, i.e.

$$d(1/\chi)/dT = 3k_B/Lg^2\mu_B^2\mu_{\text{eff}}^2.$$

This predicts a value for  $g^2\mu_{\text{eff}}^2$  of 2.76, which for  $S = \frac{1}{2}$  gives a  $g$ -factor of 1.92. This compares favourably with measured (ESR)  $g$ -factors for  $\text{Ni}^{3+}$  impurities in near-octahedral environments in oxides, which are typically around 2.1 and isotropic [11]. In our work, no diamagnetic corrections to the susceptibility have been made; these would tend to raise the value of the effective magnetic moment observed. The corresponding



**Figure 2.** Plot of  $\log_e(M/H)$  at  $H = 0.02$  T versus  $\log_e(T - T_c)$ , for the most stoichiometric  $\text{LiNiO}_2$  sample, with  $T_c$  estimated to be 6 K. Slope of straight line:  $-1.7$ .

graphs for  $\text{NaNiO}_2$  and the other sample of  $\text{LiNiO}_2$  were qualitatively similar, with intercepts of 50 K and 65 K respectively.

In figure 2 we derive an upper critical exponent for  $\text{LiNiO}_2$ , on the basis of  $\chi$  measured at 0.02 T. We assume here a value of 6 K for the Curie temperature,  $T_c$ , as with our equipment we are unable to locate it precisely. The error inherent in this is actually quite small, as it makes little difference to the position of the higher temperature points what value between 4 and 10 K is chosen. The slope of the linear region of the graph is  $-1.7$ , which agrees closely with the  $-7/4$  upper critical exponent predicted by a 2D Ising model [18]. The ESR measurements in [12] also suggest that the system should be Ising-like.

The two points closest to the Curie temperature do not conform to the line  $\chi \propto (T - T_c)^{-7/4}$ . In part this may arise from inaccuracies in the estimate of the Curie temperature, and, more importantly, from the fact that  $M$  versus  $H$  becomes increasingly non-linear in this region and so  $M/H$  will tend to underestimate the zero-field limit of  $\chi$ . This latter will move the points towards the Ising line. There is also the possibility at low temperatures of weak interlayer magnetic interactions becoming apparent, which will tend to reduce the value of the critical exponent observed, as is seen in other pseudo-2D systems [19].

The upper critical exponents may be similarly derived for the other materials. The values obtained are  $-1.7$  ( $\text{NaNiO}_2$ ) and  $-1.8$  ( $\text{LiNiO}_2$ , sample 1). A two dimensional Ising model also predicts a lower critical exponent (for the spontaneous magnetisation) of  $1/8$ , but this quantity is likely to prove extremely difficult to measure with any accuracy, as the small values for both the Curie temperature and the exponent mean that the magnetisation will saturate extremely rapidly.

In  $\text{NiO}$ , the magnetic structure is dominated by strong  $180^\circ$  Ni-O-Ni superexchange interactions which results in antiferromagnetic coupling [20]. In  $\text{LiNiO}_2$ , however, all such  $180^\circ$  interactions are absent, leaving only direct Ni-Ni interactions, and  $90^\circ$  superexchange interactions via oxygen. The former are likely to be very weak, as

photoemission measurements [21] show the d-bandwidth in this material to be very small. The latter should give rise to weak ferromagnetic interactions [22], due to intra-atomic exchange on O, provided the Ni–O–Ni bridge angle is not too large. No detailed structural studies of LiNiO<sub>2</sub> appear to have been made, but in the related material LiCoO<sub>2</sub>, the bridge angle is 95.4° [23].

As the simplest means of constructing a 2D trigonal lattice of transition metals ions in a material such as an oxide is via corner-sharing MO<sub>6</sub> octahedra (i.e. 90° M–O–M bridges), it may prove difficult to produce a real trigonal antiferromagnet. NaTiO<sub>2</sub> may still be a possibility, though, as the lower effective nuclear charge compared to Ni will result in a greater spatial extent for the 3d wave-functions and thus greater direct M–M interactions.

At this point it is worth comparing our data with that obtained in [4]. Their raw *M* versus *H* data are qualitatively similar to ours, showing a linear relation (at low applied fields) at high temperatures, becoming non-linear at low temperatures, and finally showing hysteresis and spontaneous magnetisation in zero field at 4.2 K. The non-linearity in *M* versus *H* persists to a higher temperature than in our work (up to almost 200 K) and the magnetisation values obtained at a given field are larger. In part this may be due to differences in the precise composition of the materials being studied, however. No analytical details were given in [4], save the powder diffraction pattern, and one of the starting materials used in the synthesis of LiNiO<sub>2</sub> was claimed to be Ni<sub>2</sub>O<sub>3</sub>, which is not known as a stoichiometric phase [24].

More seriously, we are at a loss to understand how, in [4], the conclusion was reached that their sample ordered ferrimagnetically below 210 K. A Curie–Weiss plot supporting this conclusion is presented (their figure 4(e)), but only one of their magnetisation curves (that at 4.2 K) shows the requisite spontaneous magnetisation. At all other temperatures, the slope of *M* versus *H* (and thus  $\chi$ ) appears to remain finite down to zero field.

In conclusion, we have shown, contrary to previous work, that the layered nickel oxides ANiO<sub>2</sub> are not suitable candidates to possess an RVB quantum liquid ground state, as the spins appear to be weakly ferromagnetically coupled, as would be expected from the available exchange pathways in this system. The measured effective magnetic moment is in line with that found for isolated Ni<sup>3+</sup> ions, and the behaviour above the Curie temperature is close to that predicted by an Ising model.

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