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Magnetic properties of the $S = 1/2$ antiferromagnetic triangular lattice $LiNiO_2$

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Abstract. We measured susceptibility, resistivity and specific heat of the $S = 1/2$ antiferromagnetic triangular lattice $LiNiO_2$. In addition to the formerly recognized characteristic temperatures T_{N1}(~210 K) and T_{N2}(~20 K), we found another characteristic temperature T_{N3}(~70 K) from the susceptibility measurement, at which three-dimensional short-range order presumably sets in at the expense of the planar frustration. In the range between T_{N1} and T_{N3}, an exponentially increasing susceptibility with decreasing temperature was disclosed, which is believed to be one of the characteristic features of the planar frustration in this system. The specific heat results revealed that the magnetic entropy gradually decreases from $R \ln 2$ without any pronounced anomalies corresponding to a long-range magnetic order down to 0.4 K. The nature of the ordering process of $LiNiO_2$ is discussed by referring these characteristic temperatures.

1. Introduction

The triangular lattice with antiferromagnetic interactions is a well-known example of a frustrating system. The simplest system is an antiferromagnetic triangular lattice of Ising spins interacting with their nearest neighbours only. Such a system is proved to have a finite entropy at absolute zero and to exhibit no long-range order at any finite temperatures [1]. This state is called the Wannier state, which contains no unit triangle with three parallel spins. In the antiferromagnetic triangular lattice of the XY or the Heisenberg spin system, the frustration can be partially lifted by rotating spins by 120° successively from site to site, which is called the three-sublattice Néel state. However, Anderson [2] suggested that the ground state of the $S = 1/2$ Heisenberg antiferromagnetic triangular lattice may be quite different from the conventional Néel state. He postulated that the ground state in this case may be a so-called resonating-valence-bond (RVB) state, which is a quantum liquid composed of randomly distributed movable singlet pairs of spins. It has been further suggested [3] that the ground state of anisotropic Heisenberg systems may also be such a RVB state, even in the Ising limit.

The electric, magnetic and crystallographic properties of the system $Li_xNi_{1-x}O$ have been the subject of several investigations. Dyer *et al* [4] suggested the possibility of preparing a complete range of solid solutions over the entire compositional range $0 \leq x \leq 0.5$. Goodenough *et al* [5] made an extensive study on the crystallographic and magnetic properties of $Li_xNi_{1-x}O$ for the entire range; they confirmed that this system can be represented by the formula $Li_x^+Ni_{1-2x}^{2+}Ni_x^{3+}O$, and suggested that Ni^{2+} unambiguously has a spin $S = 1$ and that Ni^{3+} is probably in the low-spin state of $S = 1/2$. In

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their analysis, it was assumed that the g-value is equal to two and that all Ni–O–Ni interactions are antiferromagnetic.

Hirakawa *et al* [6] pointed out that $LiNiO_2$ is suitable for a model of an $S = 1/2$ antiferromagnetic triangular lattice with an Ising-like anisotropy. $LiNiO_2$ has a modified NaCl structure in which close-packed triangular layers of each kind of atom are stacked along one of the [1 1 1] directions in the order Ni-, O-, Li-, O-, Ni-layer, and thereby that each Ni-layer is intercalated by three non-magnetic layers. It is supposed that the two-dimensional magnetic characteristics result from this structural feature of the compound. Hirakawa *et al* believed that the Ni ions in $LiNiO_2$ are trivalent and that the electronic configuration is a $3d^7$ high-spin state, which is equivalent to that of Co^{2+}. Lines [7] suggested that the ground state of the Co^{2+} ion in a trigonal field is a low-lying Kramers doublet and that the ion behaves like a fictitious spin $S = 1/2$ with an Ising-like anisotropy.

It has been pointed out from magnetic susceptibility measurements [6] and ESR measurements [8] that the compound exhibited successive changes in the magnetization processes at $T_{N1} \approx 210$ K and $T_{N2} \approx 20$ K. The compound was paramagnetic above T_{N1} and followed the Curie–Weiss law. Below T_{N1}, the magnetization M was non-linear to the external field H as is often the case in ferrimagnets and the relation $M \propto H^{1/\delta}$ was suggested. Contrary to a conventional ferrimagnet, the magnetization increased steeply with decreasing temperature. Below T_{N2}, the rate of increase became smaller and the magnetization became hysteretic. However, it could not be completely saturated even in strong magnetic fields at 4.2 K. Nevertheless, no magnetic order was confirmed between 1.4 K and 300 K by their neutron scattering measurements [6] performed in 0 and 65 kOe. On the basis of these results, it has been concluded that some kind of order may occur but no spatial antiferromagnetic lattice is formed at low temperatures though the compound behaves like a ferrimagnet in external fields. On the other hand, NMR experiments [9] at 4.2 K detected a small internal field suggesting a magnetically ordered state.

Recently, Kuiper *et al* [10] showed by oxygen K-edge x-ray absorption spectroscopy (XAS) that the holes compensating the Li^+ impurity charge in $Li_xNi_{1-x}O$ ($0 \leqslant x \leqslant 0.5$) are located primarily in the O 2p state rather than in the previously assumed Ni 3d state. They proposed that these O 2p holes have a large antiferromagnetic exchange interaction ($J \approx 0.3$ eV) with neighbouring Ni^{2+} ($3d^8$) spins and that in the ordered phase all Ni ions have $S = 1$ up spins and O 2p holes $S = 1/2$ down spins. Accordingly, their model is equivalent to a low-spin Ni^{3+} magnet on a macroscopic scale.

In order to clarify the nature of the ordering process in $LiNiO_2$, we measured the specific heat from 0.4 K to 300 K, as well as the DC susceptibility and magnetization with a SQUID susceptometer from 6 K to 400 K in various magnetic fields. We paid special attention to sample quality because it has strong effects on the frustration, which is expected to play an important role in antiferromagnetic triangular lattices. We have also investigated the effects of the frustration on the process of spin ordering by partially substituting non-magnetic ions for Ni^{3+} ions at random.

2. Experiment

2.1. Sample preparation

We have tried several methods of preparation of sintered samples and have obtained satisfactory results with the following method proposed by Thomas *et al* [11]. Powders

Table 1. Observed and calculated intensities for the sample KH114 with $a_H = 2.881$ Å and $c = 14.198$ Å. In the calculations, $K_\alpha = 1.54180$ Å was assumed for $2\theta < 20°$ and $K_{\alpha 1} = 1.54056$ Å for $2\theta > 20°$.

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}	I_{calc}
0	0	3	18.72	18.749	1000	1000
1	0	1	36.53	36.530	267	327
1	0	4	44.34	44.336	534	577
0	1	5	48.52	48.526	80	127
0	1	8	64.36	64.360	114	136
1	1	0	64.64	64.640	100	113

of Li_2O_2 and NiO were thoroughly mixed in an argon glove box and pelletized at the pressure of 250 kgf cm^{-2}. Pellets of 12 mm diameter were placed on an alumina boat in a tubular furnace of Quartz glass. The pellets were heated up to 850 °C at a rate of 1 °C min^{-1} under a stream of pure dried oxygen passed through liquid nitrogen, and maintained for 24 h ~ 48 h before cooling to room temperature at a rate of 1 °C min^{-1}. Since a small amount of reagents and impurity phases were sometimes detected after the first firing, we repeated this a few times until all the peaks of foreign phases on the x-ray diffraction pattern completely disappeared.

For the samples prepared this way, the observed peak intensities were in good agreement with the calculated ones, as shown in table 1, where several main peak intensities are computed. When fired in open air at higher temperatures, however, the relative intensities differed from the calculated ones, even if the peaks of foreign phases were not present. It was found that a prolonged firing under such conditions gave a pattern similar to that for NiO, suggesting a progressive loss of Li from $LiNiO_2$ and a substitution of Ni for Li. This result is consistent with that of Thomas *et al*: the higher lithium contents are attainable only under a moisture-free reaction condition because LiOH has a significant vapour pressure above 800 °C.

The crystal structure of $LiNiO_2$ is called the α-$NaFeO_2$ type, which has a rhombohedral $R\bar{3}m$ symmetry. We indexed the diffraction peaks taking the conventional hexagonal unit cell. By using a least-squares program, cell parameters were determined for all samples. In this article, experimental results on only three of them are reported. Their compositions were estimated using the relationship between the lithium content and the unit cell volume, established by Goodenough *et al* [5]. The compositions of the samples KH112, KH113 and KH114 were found to be $Li_{0.904}Ni_{1.096}O_2$, $Li_{0.893}Ni_{1.107}O_2$ and $Li_{0.944}Ni_{1.056}O_2$, respectively.

2.2. AC susceptibility

AC susceptibility, χ_{AC} was measured in an AC field of 100 mOe rms at 123 Hz without external fields, which thus probes the initial susceptibility.

The results for KH112, KH113 and KH114 are shown in figure 1. These samples were prepared under almost the same conditions except for the quality of the starting material Li_2O_2. It is known that Li_2O_2 gradually changes to LiOH and/or $LiOH \cdot H_2O$ with time, by absorbing moisture. We found that a huge peak appeared between 30 K and 80 K depending strongly on the sample quality. In fact, as peaks of foreign phases

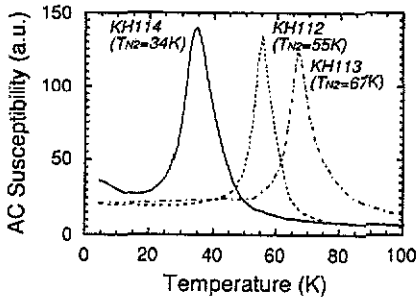

Figure 1. Temperature dependence of the AC susceptibility of KH112 (-----), KH113 (—·—) and KH114 (——) measured in an AC field of 100 mOe at 123 He without external fields.

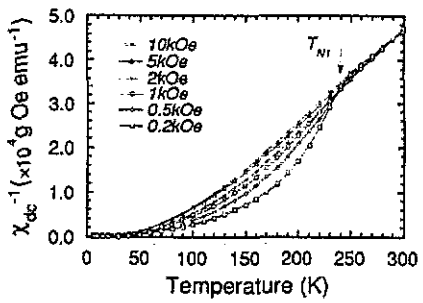

Figure 2. χ_{DC}^{-1} versus T of $LiNiO_2$ measured in uniform magnetic fields at 200 Oe (□), 500 Oe (◇), 1 kOe (○), 2 kOe (+), 5 kOe (△), and 10 kOe (×).

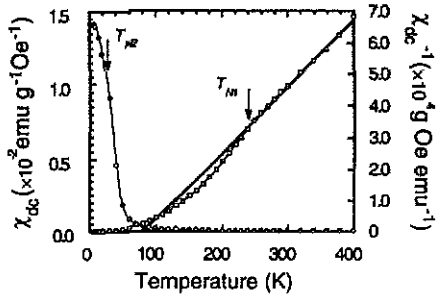

Figure 3. Temperature dependence of the DC susceptibility of $LiNiO_2$ measured in 1 kOe. The data are plotted as χ_{DC} versus T (○) and χ_{DC}^{-1} versus T (□).

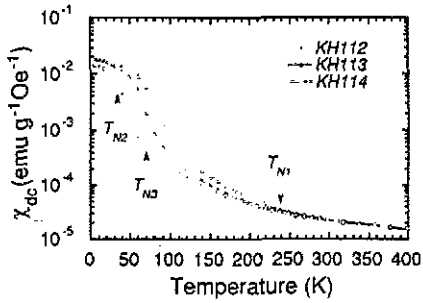

Figure 4. Log χ_{DC} versus T of KH112 (×), KH113 (△) and KH114 (○) measured in 1 kOe.

on the x-ray diffraction pattern disappeared and the relative intensities approached the calculated ones, the peak of χ_{AC} shifted to lower temperatures. Note that monitoring the peak temperature served as another way of checking the sample quality, or the deviation from the stoichiometry, in addition to the x-ray diffraction.

2.3. DC susceptibility

Measurements of the DC susceptibility, χ_{DC}, were made from 400 K down to 6 K in uniform magnetic fields between 200 Oe and 10 kOe, with a SQUID susceptometer. We define χ_{DC} as M/H where M is magnetization and H is magnetic field.

The results for $LiNiO_2$ are shown in figures 2 and 3. Hirakawa *et al* observed that the χ_{DC}^{-1} decreased on a hyperbolic curve characteristic to ferrimagnets and rapidly approached zero around 210 K, which they defined as T_{N1}. The present result, however, indicates that the χ_{DC}^{-1} deviates abruptly from the Curie–Weiss law at 240 K and gradually approaches zero with decreasing temperature. On the basis of the result, we redefine the temperature as T_{N1} where χ_{DC}^{-1} deviates from the Curie–Weiss law.

The susceptibility above T_{N1} closely follows the Curie–Weiss law with the Curie constant of $4.761 \times 10^{-3} \pm 9.5 \times 10^{-5}$ emu K g^{-1} Oe^{-1} and the Weiss temperature of 79.25 ± 4.75 K. Provided that only Ni ions in $LiNiO_2$ carry magnetic moments and that

the orbital angular momentum, L, is frozen, the spin quantum number, S, is estimated at 0.5455. We assumed that the g value is equal to 2.1, which was obtained in the ESR measurements [8].

The point of inflection on the χ_{DC} versus T curve at about 35 K is called T_{N2}, as before. It should be noted here that this temperature coincides with the temperature where the huge peak appears on the χ_{AC} curve.

In order to look into the temperature dependence in more detail, the data are replotted as log χ_{DC} against T as shown in figure 4. It can be seen that the log χ_{DC} increases almost linearly from $T_{N1} \approx 240$ K down to about 70 K and then increases even faster. This temperature at which the abrupt change of slope takes place is called T_{N3}.

It is important to note that T_{N2} and T_{N3} were strongly affected by the sample quality though T_{N1} was little affected, as clearly demonstrated for the three samples in the figure. We believe that the exponential increase of χ_{DC} between T_{N1} and T_{N3} is a result of strong frustration. This point will be further discussed below.

2.4. *Time dependence of χ_{DC}*

Upon realizing considerably larger susceptibilities in field-cooling than zero-field-cooling, we have investigated the response of the magnetization, M, to abruptly changed fields, and have found a relaxation phenomenon with a long time constant below T_{N2}, which reached, for example, at least 6 h at 6 K. The results for $LiNiO_2$ are shown in figure 5. The reported magnetic hysteresis [6] below T_{N2} is presumably attributed to this relaxation phenomenon.

2.5. *Field dependence of magnetization*

Since below T_{N2} the field induced magnetization changes with a long relaxation time, it is difficult to measure a magnetization curve directly at low temperature. Therefore we deduced the field dependence of the magnetization in a thermal equilibrium state using the results of χ_{DC} versus T measurements for different external fields. In the case of cooling in field, the data were in accord with those in increasing temperature. Thus we could assume that the sample was in a thermal equilibrium state and that the magnetization was independent of time. The M versus T curves thus obtained for $LiNiO_2$ are shown in figure 6.

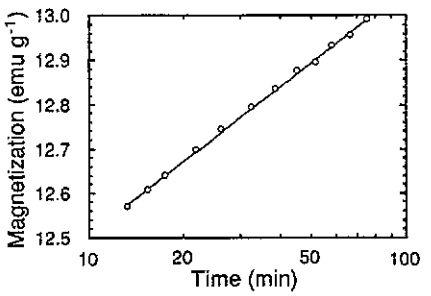

Figure 5. Time dependence of the magnetization of $LiNiO_2$ when an external field of 1 kOe was abruptly applied at 6 K.

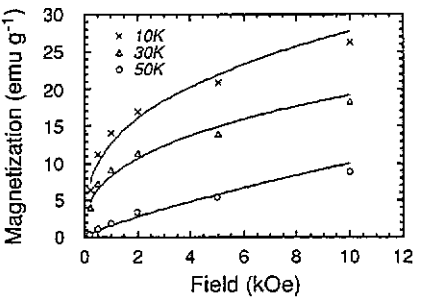

Figure 6. Field dependence of the magnetization of $LiNiO_2$ at 10 K (×), 30 K (△) and 50 K (○), deduced from the DC susceptibility measurements for different external fields.

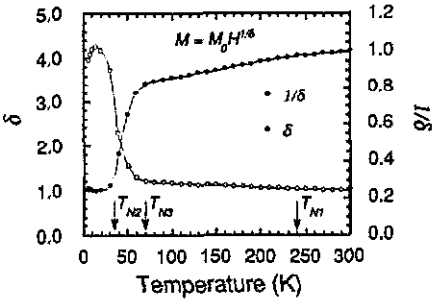

Figure 7. Temperature dependence of the fitting parameter δ (○) and $1/\delta$ (●) in the expression of $M = M_0 H^{1/\delta}$.

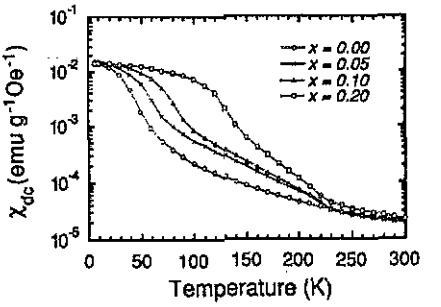

Figure 8. Log χ_{DC} versus T plots of $LiNi_{1-x}Cu_xO_2$ for $x = 0.00$ (○), 0.05 (×), 0.10 (△) and 0.20 (□) measured in 1 kOe.

For a quantitative discussion of the field dependence, we fitted the data to the following two expressions using a least-squares method:

$$M(t) = M_0 + M_1 \log(H) \tag{1}$$

$$M(t) = M_0 H^{1/\delta}. \tag{2}$$

It seems that the latter relation fitted the data very well for the whole temperature range, while the former fitted fairly well only below 50 K.

The fitting parameter δ, for $LiNiO_2$ is plotted as a function of temperature in figure 7, where the aforementioned four temperature regions derived from figure 4 are clearly demonstrated: δ is almost unity above T_{N1} as expected for a paramagnet; it deviates from unity below T_{N1}, slowly approaching 1.3 around 100 K; it starts increasing rapidly at T_{N3} and slows down again around T_{N2}, finally reaching 4 at the lowest temperatures.

2.6. $LiNi_{1-x}Cu_xO_2$

In order to investigate the effects of disorder introduced on the triangular lattice of Ni by substitution, we also measured the temperature dependence of the susceptibility of $LiNi_{1-x}Cu_xO_2$. Cu ions seem to enter as non-magnetic Cu^{3+} ions at low concentrations at least. The results for $x = 0.00$, 0.05, 0.10 and 0.20 are shown in figure 8.

The temperature dependence of χ_{DC} is very much influenced by the Cu substitution. Results are summarized as follows:

(i) T_{N1} is little influenced but the χ_{DC} below T_{N1} increases more rapidly with the substitution;

(ii) T_{N3} and T_{N2} shift to higher temperatures on substitution;

(iii) the low temperature magnetization tends to decrease with increasing Cu concentration.

2.7. *Specific heat*

Specific heat measurements were made from 0.4 K to room temperature without external fields by using the adiabatic heat-pulse method. The result for $LiNiO_2$ is shown in figure 9. It is remarked here that below 1 K the specific heat, C_p, varies approximately as T^2 and that no pronounced anomalies except a small hump around 6 K appear in the investigated temperature range.

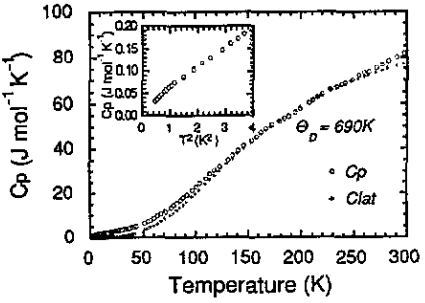

Figure 9. Temperature dependence of the specific heat (O) and the lattice specific heat (+) of $LiNiO_2$ without external fields. The inset shows the quadratic T dependence at the lowest temperatures.

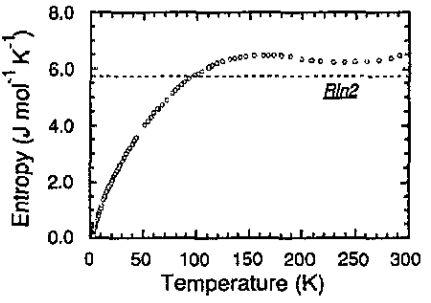

Figure 10. Temperature dependence of the magnetic entropy, deduced from the results shown in figure 9.

The magnetic contribution, C_{mag}, to the specific heat can be found by subtracting the lattice specific heat from the measured one, if the other contributions can be neglected. In fact, from our electrical resistivity and low temperature specific heat measurements, it was confirmed that $LiNiO_2$ is a semiconductor with a small gap of about 0.17 eV at room temperature and the compound does not possess the T-linear electronic contribution to C_p [12].

The lattice contribution was estimated for $LiNiO_2$ by assuming the Debye model with the Debye temperature, Θ_D, of 690 K. The Debye temperature was determined such that an overall best fitting above about 200 K was obtained without exceeding the experimental values of C_p at any temperatures. This assumption is corroborated by the fact that the Debye model fits the specific heat [12] of the isostructural compound $LiCoO_2$, which was confirmed to be a van-Vleck paramagnet from the susceptibility measurement [12], fairly well. The Debye temperature obtained by fitting the data of $LiCoO_2$ between 30 and 250 K was 800 K, which was too high to directly simulate the lattice specific heat for $LiNiO_2$.

The magnetic entropy obtained by integrating C_{mag}/T is plotted as a function of temperature in figure 10. The error was estimated to be about ± 0.5 J mol^{-1} K^{-1} at 300 K, which approximately corresponds to about ± 5 K in the error for the Debye temperature determined above. We note here that the variation above about 200 K would be a phenomenon due to an inaccurate calibration of our calorimeter rather than an inappropriate subtraction of the lattice contribution. Nevertheless one can see that the full entropy of about $R \ln 2$ is consistent with the $S = 1/2$ state of Ni^{3+} and that the entropy gradually decreases without any noticeable anomalies corresponding to long-range orders in the magnetic entropy down to 0.4 K.

3. Discussion and summary

Frustration is supposed to be very sensitive to the sample quality because it results from a subtle balance of interactions among spins on the triangular lattice. As noted in the preceding section, we found that both T_{N2} and T_{N3} were reduced for better quality samples, while T_{N1} was unchanged. It is between T_{N1} and T_{N3} that the susceptibility was exponentially dependent on the temperature and decreased as the sample quality was

improved. From these results, it would be reasonable to assume that any disorder on the triangular lattice impedes the frustration which keeps spins from ordering between T_{N1} and T_{N3}. This assumption is consistent with the susceptibility data of $LiNi_{1-x}Cu_xO_2$, for which we found the disorder created by substitution raised both T_{N3} and T_{N2}, and enhanced the susceptibility below T_{N1}.

We now discuss the spin state of each temperature region derived from the present results as follows:

(i) For the high temperature state ($T_{N1} < T$) it is confirmed from the susceptibility measurement that $LiNiO_2$ behaves like a Curie–Weiss paramagnet with $S = 0.546$, which is consistent with the almost full magnetic entropy of $R \ln 2$ derived from the specific heat measurement. The Weiss temperature is estimated to be 79.3 K.

(ii) For the intermediate state I ($T_{N3} < T < T_{N1}$) the magnetization increases exponentially with decreasing temperature and becomes non-linear to external fields. In addition, it is strongly affected by the sample quality as mentioned above. The magnetic entropy starts decreasing gradually from about 150 K and about 20% of the full magnetic entropy is lost in this region. These results imply that we enter a scheme of a frustrated spin state of planar short-range order on the triangular lattice.

(iii) For the intermediate state II ($T_{N2} < T < T_{N3}$) the magnetization strongly increases from T_{N3}, though no noticeable anomalies corresponding to long-range order are found in the magnetic entropy. About half of the full entropy has been lost before reaching T_{N2}. It is possible that in this temperature range, three-dimensional short-range order is induced by interplanar correlations. This should be verified by other experimental techniques such as small-angle neutron diffraction experiments.

(iv) For the low temperature state ($T < T_{N2}$), below T_{N2}, the magnetization tends to saturate and shows relaxation phenomenon with a long time constant. An appreciable amount of the magnetic entropy still remains at T_{N2} but gradually disappears without pronounced anomalies related to long-range orders. It is reasonable to presume that a kind of frozen spin state is realized rather than a long-range-ordered state. However, this frozen spin state would be different from an ordinary spin glass because of the quadratic temperature dependence of the specific heat rather than linear one as expected for spin glasses. So, this frozen spin state may be a new low-temperature state characteristic to frustrated systems.

Recently, Yoshizawa *et al* [13] performed neutron diffraction measurements on the same sample of $LiNiO_2$ as used in the present study. They revealed the development of ferromagnetic short-range correlations in forward scattering below T_{N1}. They also suggested from the temperature dependence of newly discovered diffuse scattering that a frozen spin pattern similar to a spin glass phase is realized below T_{N2}. Goto *et al* [14] made the measurements of magnetization versus magnetic field up to 100 T at 4.2 K with a pulsed magnet. They observed no anomalies above 40 T where the magnetization is saturated to approximately 1.0 μ_B per Ni. These results seem to support our interpretation of the spin state based on our data.

Hirakawa *et al* [6, 15] tried to understand the low-temperature behaviour of $LiNiO_2$ in the framework of the RVB theory. However, the RVB state has been theoretically studied so far almost exclusively about the ground state and the finite temperature properties are not well enough known at present. Accordingly, we merely compare our experimental results with theoretical models for classical spin systems which have been extensively studied.

Antiferromagnetic triangular lattices of classical spins have been theoretically inves-

tigated by many authors and many interesting results concerning ordering processes have been found. Mekata [16] has shown that Ising antiferromagnetic triangular lattice with next-nearest-neighbour (NNN) interactions exhibits two successive phase transitions and the low-temperature phase is ferrimagnetic. For the intermediate phase, he postulated a partially disordered (PDO) state consisting of one paramagnetic and two antiferromagnetic sublattices. His work has been extended by many other authors [17] and it has been suggested that such a PDO state is unstable and each sublattice alternates with time and space because of the triangular lattice symmetry. Miyashita and Kawamura [18] examined an anisotropic Heisenberg model by taking into account only nearest-neighbour (NN) interactions with a Monte Carlo simulation and found two successive transitions due to orderings of z component and of xy component. They suggested that the intermediate phase is a short-range-ordered state in which the local spin configuration may be the PDO state. According to these two models, magnetic Bragg peaks are expected in neutron diffraction at low temperatures, which is, however, inconsistent with the experiments [6, 14]. Besides, these models predict cusp-like anomalies in specific heat at the transition temperatures, whereas we have not found such anomalies in the present study. Accordingly, it appears that $LiNiO_2$ has properties quite different from these theoretical predictions, though they seem to be consistent with the results of hexagonal ABX_3-type compounds such as $CsCoCl_3$ [19], in which antiferromagnetically interacting magnetic chains form a triangular structure.

On the other hand, Matsubara and Inawashiro [20] have studied an anisotropic antiferromagnetic Heisenberg model for a hexagonal close packed lattice with ferromagnetic NNN planar interactions and three-dimensional NN interactions. They found that with decreasing temperature, a two-dimensional paramagnetic state enters the three-dimensional incommensurate short-range-ordered state. Finally, at low temperatures, it reaches a non-periodic frozen spin state in the case of a large Ising-like anisotropy, while a three-dimensional incommensurate long-range-ordered state may occur when anisotropy is small. If the frozen spin state observed in the present study is not simply due to defects on the triangular lattice, their model appears to have something to do with our interpretation for the spin ordering processes in $LiNiO_2$. It would, then, be interesting to check whether these theoretically proposed states really represent the states found in the present work.

Lastly, we give brief comments on the electronic state of $LiNiO_2$ by referring to the results of the present study and more recent neutron diffraction experiments. Several models of different spin state for the Ni ion have been proposed to explain some particular experimental results. Those models may be summarized as follows:

(i) Ni^{3+} low-spin state: $S = 1/2$, $g = 2$ (isotropic);

(ii) Ni^{3+} high-spin state [6]: fictitious spin of Kramers doublet of $S = 1/2$, $g_{\parallel} = 7.1$, $g_{\perp} = 2.1$ (Ising-like anisotropy);

(iii) Ni^{2+} antiferromagnetically coupled with O 2p holes (exchange constant $J_{Ni\text{-}O} \sim 0.36$ eV) [10]: Ni^{2+}: $S = 1$ up, O 2p holes: $S = 1/2$ down.

If Ni^{2+} ions are more strongly coupled with O_{2p} holes than with neighbouring Ni ions via such a large exchange constant as proposed in the model (iii), a long-range antiferromagnetic state between Ni and O-layers may be expected at a relatively high temperature. However, we did not observe any long-range ordered state down to 0.4 K in our specific heat measurement, as discussed above. This fact is also supported by the recent neutron diffraction experiment of Yoshizawa *et al* [13].

According to model (ii), on the other hand, an *up-up-down* ferrimagnetic phase is

expected in an external magnetic field to be consistent with the saturation magnetization of $1\mu_B$ per Ni found in the high field magnetization experiment [14]. Moreover, a metamagnetic transition is supposed to take place in high fields for such a ferrimagnetic state, but no anomalies on the magnetization curve have been detected up to 100 T after reaching about $1\mu_B$ per Ni around 40 T [14].

The Ni^{3+} low-spin state of model (i), however, seems to be consistent with all the results of the present study and both the neutron diffraction [13] and the high field magnetization experiments [14]. Consequently, it seems at present reasonable to assume that $LiNiO_2$ is a system of frustrating Ni^{3+} ions of low-spin state. It is important to investigate this interesting compound further by other experimental means.

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