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Spin-glass freezing in the $S=1$ antiferromagnetic Heisenberg chain $NiC_2O_4 \cdot 2[(2\text{-methylimidazole})_x (H_2O)_{1-x}]$

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We report the results of dc, linear ac, and nonlinear ac magnetic susceptibility measurements on the $S=1$ linear-chain Heisenberg antiferromagnet $NiC_2O_4 \cdot 2L_xL'_{1-x}$ [$L=$2-methylimidazole(2MIz); $L'=H_2O$] ($0.045 \leqslant x \leqslant 0.49$). We have observed spin-glass freezing in the compounds with $x \geqslant 0.078$. On the other hand, no spin-glass freezing has been observed in $Ni_{1-x}Zn_xC_2O_4 \cdot 2L$ ($L=$2MIz) in the range $0 \leqslant x \leqslant 0.29$. This means that the spin-glass freezing is not caused by shortening the length of magnetic sites in $\cdots$Ni-C_2O_4-Ni$\cdots$ chains, but is caused by structural defects on the chains in $NiC_2O_4 \cdot 2L_xL'_{1-x}$. A possible origin of this spin-glass freezing is discussed. [S0163-1829(97)06710-6]

The great interest in linear-chain Heisenberg antiferromagnets (LCHA's) has been strongly renewed after a surprising conjecture by Haldane[1] that the LCHA's with integer spin values have an energy gap between the disordered ground state and the first excited one, while those with half-odd-integer values have no energy gap. A lot of theoretical and experimental studies have been done on LCHA's with $S=1$ and the validity of this conjecture has been accepted, at least, for the case of $S=1$. One of the most attractive findings in the $S=1$ LCHA's is the presence of $S=1/2$ degrees of freedom induced at the ends of finite chains. A quasifourfold degenerate ground state, which can be viewed as arising from the $S=1/2$ degrees of freedom at both ends in a finite chain, was shown to exist from an exact diagonalization of an $S=1$ LCHA with open boundary conditions.[2] From the discussion based on the valence-bond-solid model by Affleck *et al.*,[3] we can intuitively understand the appearance of the $S=1/2$ degrees of freedom. The existence of the $S=1/2$ degrees of freedom was demonstrated experimentally in the $S=1$ LCHA compound $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, abbreviated as NENP,[4] followed by the experiments on many other $S=1$ LCHA compounds.[5–8]

If there is no interaction between the $S=1/2$ degrees of freedom, the system should exhibit paramagnetism down to zero K.[9] When an interaction between the $S=1/2$ degrees of freedom exists, we expect that the system will exhibit a magnetic ordering at a finite temperature. Recently, we reported the observation of spin-glass transition in a nominally pure single crystal of NENP (Refs. 10 and 11) and proposed the following mechanism for the occurrence of the spin-glass transition. In our nominally pure NENP, the moments are induced at the chain ends probably by structural defects. Here, we assume that such defects are created by a displacement of intervening anions ClO_4^- towards the chain. Then, there will be a possibility of having a 90° exchange bond between the neighboring Ni atoms in the chain. This bonding gives a ferromagnetic exchange interaction, whereas antiferromagnetic interactions between the neighboring Ni atoms exist at other sites in the chain. Accordingly, ferromagnetic and antiferromagnetic bonds are distributed randomly in the chain. Moreover, the interchain exchange interaction is expected to be stronger than that in an ideal sample. This latter exchange bond causes a frustration as described in Ref. 11. However, it is very difficult to control the number of crystal defects in order to prove this mechanism in NENP. $NiC_2O_4 \cdot 2L$ [$L=$1,2-dimethylimidazole (DMIz), 2-methylimidazole (2MIz) or H_2O] is a quasi $S=1$ LCHA and has been studied to investigate the impurity effects in the $S=1$ LCHA.[12] In order to verify the mechanism proposed in the previous paper,[10] we study powder samples of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ ($L=$2MIz, $L'=H_2O$) in which the number of structural defects can be controlled by the ratio of L to L'. In the present paper, we report the results of the systematic studies on the spin-glass freezing in $NiC_2O_4 \cdot 2L_xL'_{1-x}$ ($L=$2MIz, $L'=H_2O$).

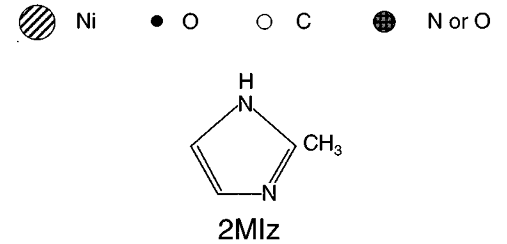

FIG. 1. Schematic view of the crystal structure of $NiC_2O_4 \cdot 2L$ [$L=$2-methylimidazole (2MIz) or H_2O]. Structure of 2MIz is depicted below it.

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$NiC_2O_4 \cdot 2L$ crystallizes in the monoclinic system and belongs to a family of metal oxalate complexes $MC_2O_4 \cdot 2L$ (M=Fe, Co, Ni, or Zn), where L represents DMIz, 2MIz, or H_2O.[13] The structure consists of $\cdots$Ni-C_2O_4-Ni$\cdots$ chains as shown in Fig. 1 and imidazole or water derivatives are placed at axial positions. Ni ions are surrounded by an octahedron formed by four oxalate oxygen atoms and two nitrogen atoms (2MIz, DMIz) or oxygen atoms (H_2O) from the derivatives. As reported earlier in Ref. 13, the temperature dependence of susceptibility of all these $NiC_2O_4 \cdot 2L$ shows a rounded maximum around 40 K (41 K for $L=H_2O$, 45 K for L=2MIz and 47 K for L=DMIz). Thus, the intrachain exchange interaction between Ni^{2+} spins via the nearly 180° Ni-C_2O_4-Ni bond is determined to be antiferromagnetic. The powder samples of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) were grown from a reaction of water solutions of $NiCl_2$ (99.99%), 2-methylimidazole and $Na_2C_2O_4$ with the amount ratio of 1:x:1. The real composition ratio x was determined by chemical analysis.

In the following, we present the results of magnetic susceptibility measurements on the powder samples of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$). The dc and linear ac susceptibilities were measured with a SQUID magnetometer (Quantum Design's MPMS2). Special care was taken to reduce the magnetic field at the sample position. The nonlinear ac susceptibility was measured with a Hartshorn-type bridge installed at Chiba University.

Figure 2 shows the temperature dependence of dc susceptibilities (magnetization/applied magnetic field) of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with designated composition ratio x for zero-field-cooled (ZFC) and field-cooled (FC) measurements. A marked difference between FC and ZFC measurements begins to appear in the sample with $x=0.078$, whereas no difference between them is observed for $x=0.045$. A cusp is observed in the ZFC measurement for the samples with $x \geqslant 0.23$ and moves to higher temperature sides with increasing the composition ratio x. From the chemical analysis of the samples used in the measurement, we found that the concentration of transition elements other than Ni is below about 0.02 wt. %. Since the susceptibility of $NiC_2O_4 \cdot 2L$ (L=2MIz or H_2O) shows a steep decrease below around 40 K as reported in Ref. 13, we believe that the increase of susceptibilities in the present systems at low temperatures comes from the $S=1/2$ degrees of freedom at the chain ends. Moreover, rapid increase below around 20 K for the samples with $x \geqslant 0.078$ means that an interaction between the $S=1/2$ degrees of freedom exists. In addition, there is an abrupt increase in χ as x changes from 0.23 to 0.49. This means that an increase of the number of interacting bonds among short segments ($\leqslant 2\xi$) in the neighboring chains causes an abrupt increase in χ, because the spins at chain ends in long chains ($>2\xi$) behave independently. We cannot, however, explain the increase in χ quantitatively yet.

Figure 3(a) shows the temperature dependence of the real (χ') and imaginary (χ'') parts of the linear ac susceptibility for the sample with $x=0.49$ for different dc bias fields superposed on the ac field. A cusp is seen in the temperature dependence of χ' in zero dc field. The cusp broadens with increasing dc bias field, which is commonly seen in spin-glass systems. We have also measured the linear ac susceptibilities for various frequencies as shown in Fig. 3(b). The position of the cusp in χ' moves to high temperature side with increasing frequency as commonly observed in spin glasses. The frequency shift of T_f which is defined as the maximum in χ' is investigated and $\Delta T_f/[T_f\Delta(\log_{10}\omega)]$ is obtained as ~ 0.01, which is close to that in metallic spin glasses and slightly smaller than those in other insulating spin glasses.[14] In Fig. 3(b), χ'' decreases with increasing frequency as opposed to that in the spin-glass system like $(Er_xSr_{1-x})S$ (Ref. 15) or $Fe_{10}Ni_{70}P_{20}$.[16] The behavior of χ'', however, is similar to that in the two-dimensional Ising spin-glass system $Rb_2Cu_{1-x}Co_xF_4$.[17] The χ'' behavior in $Rb_2Cu_{1-x}Co_xF_4$ was explained on the basis of scaling the susceptibility in the frequency domain according to activated dynamics from the droplet model.[18] The linear ac suscepti-

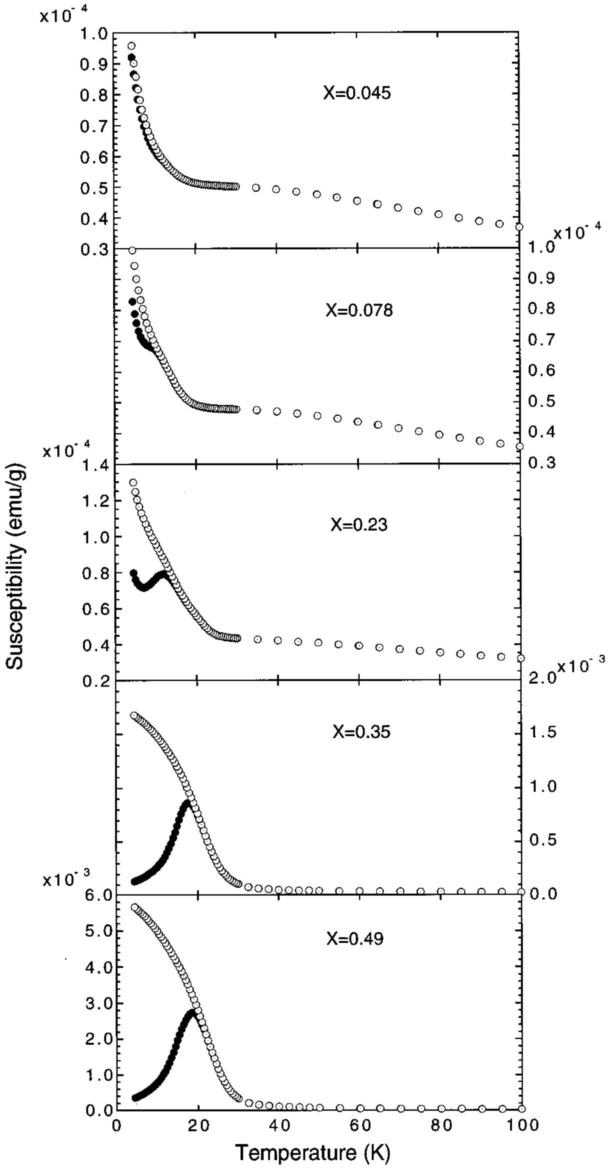

FIG. 2. Temperature dependence of the dc susceptibility in powder samples of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with designated composition ratio x. Open and solid circles show the experimental data for field-cooled (FC) and zero-field-cooled (ZFC) measurements, respectively.

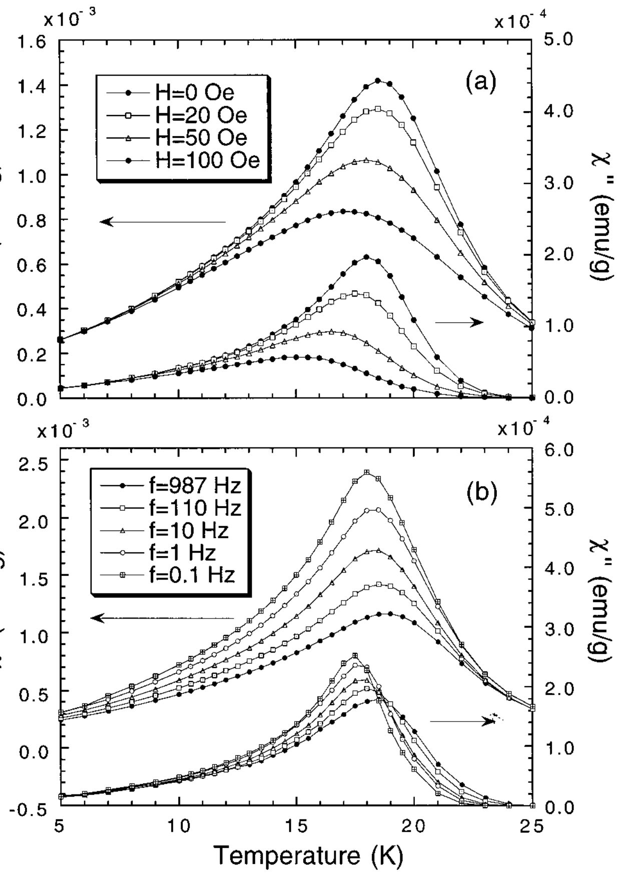

FIG. 3. (a) Temperature dependence of real (χ') and imaginary (χ'') parts of ac susceptibility in $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with $x=0.49$ for various dc fields superposed on the ac field. Solid lines are guides to the eyes. (b) Temperature dependence of ac susceptibility in the same sample for designated frequencies.

bilities of other samples with $x \geqslant 0.23$ exhibit the same behavior as those observed in this sample.

In order to obtain conclusive evidence for spin-glass transition, we have measured the nonlinear ac susceptibility of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with $x=0.49$. As was predicted theoretically by Suzuki[19] and confirmed experimentally by Chikazawa *et al.*,[20] the second component (χ_2^t) of the nonlinear susceptibility in spin glasses diverges to $-\infty$ at the freezing temperature (T_f). As is seen from Fig. 4, the temperature dependence of $-\chi_2^t$ of our sample shows an anomalous increase when T_f is approached from both sides. The same behavior of nonlinear ac susceptibility was observed in the sample with $x=0.35$, but it was not observed in the samples with $x \leqslant 0.23$ probably because of small signal intensities. From the experimental results of the systematic change of bifurcation of FC and ZFC dc susceptibilities and ac and nonlinear ac susceptibilities, we conclude that a spin-glass transition takes place in $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with $x \geqslant 0.078$.

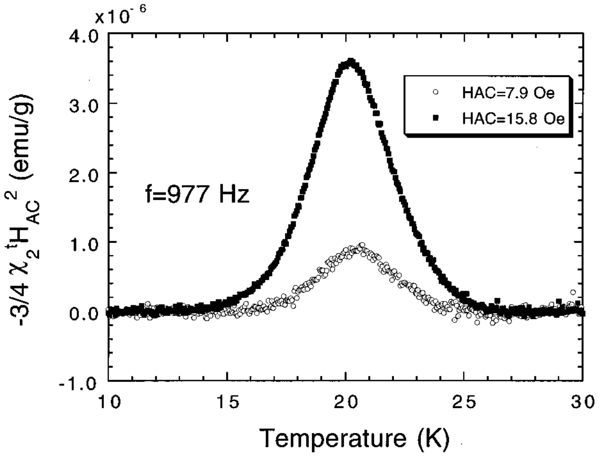

FIG. 4. Temperature dependence of nonlinear ac susceptibility (χ_2^t) of $NiC_2O_4 \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=H_2O$) with $x=0.49$ for the ac fields 7.9 Oe and 15.8 Oe.

Before discussing a possible origin of spin-glass transition in the present systems, we would like to clarify the effect of structural defects on spin-glass freezing. For this purpose, we have measured the dc susceptibilities of $Ni_{1-x}Zn_xC_2O_4 \cdot 2L$ (L=2MIz) with x up to 0.29 under the expectation that the substitution of Zn for Ni does not affect the chain structure, because the size of Ni^{2+} ion (0.84 Å) is close to that of Zn^{2+} one (1.16 Å). The results show no difference between the ZFC and FC measurements and the susceptibility increases with decreasing temperature below around 15 K due to the $S=1/2$ degrees of freedom induced at the Ni sites neighboring Zn atoms. This means that only the shortening of the chains does not cause the spin-glass freezing.

In addition to the effect mentioned above, we have to consider the chain length, because we do not observe spin-glass freezing in our Ni oxalate sample with $x=0.045$. A quantum Monte Carlo calculation study[21,22] made on an $S=1$ finite LCHA showed that a staggered moment with $S=1/2$ appears at the chain ends and it decays exponentially with the correlation length $\xi \sim 6$ which is the same as that in the bulk. It was also argued that the edge spins at both ends behave independently in a sufficiently long chain, but they interact with each other in a short chain. This argument is applicable to the case of our Ni oxalate samples, because we have observed spin-glass transition in the samples with $x \geqslant 0.078$, which means the average length is shorter than two times of the length of ξ (~ 12). Thus, the existence of a large amount of short chains of length below 2ξ becomes one of the necessary conditions for spin-glass transition.

Now let us discuss a possible origin of the spin-glass transition in our samples. It is pointed out that the dipole-dipole interaction alone cannot explain the relatively high freezing temperature. Then, we should take into account the exchange interaction as an origin of the spin-glass. Since our samples do not contain any detectable magnetic impurities, the moments are induced at the ends of finite chains by structural defects. Here, we assume that such defects are created by a displacement of 2MIz derivative towards the chain that pushes away Ni atoms, because the size of 2MIz molecule (~ 3 Å) is very different from that of water (~ 1.5 Å). Hence, there will be a possibility of having a 90° exchange bond between the neighboring Ni atoms in the chain. We expect that this arrangement will give a ferromagnetic exchange interaction[23,24] between the spins at the sites of crystal defects. These ferromagnetic bonds are distributed randomly in the chains. However, the randomly distributed ferro- and antiferromagnetic bonds in an open chain do not cause frustration in the system. At the site where a Ni atom is pushed away, the interchain exchange interaction will be much stronger than those at other sites. Randomly distributed ferro- and antiferromagnetic exchange bonds in the chain and the strong interchain exchange interaction at the sites of structural defects cause a frustration as demonstrated in Ref. 11.

In conclusion, dc, linear ac, and nonlinear ac susceptibility measurements on powder samples of $\mathrm{NiC_2O_4} \cdot 2L_xL'_{1-x}$ (L=2MIz, $L'=\mathrm{H_2O}$) with $x \geqslant 0.078$ show clearly spin-glass freezing of the moments at the chain ends created by structural defects. Although the above discussion may not be sufficient for the origin of spin-glass transition, we can conclude that structural defects in the $\mathrm{NiC_2O_4} \cdot 2L_xL'_{1-x}$ cause a spin-glass transition. We hope this experimental work will stimulate further theoretical studies.

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