

# Magnetic Transition in the Perovskite Ba<sub>2</sub>CoNbO<sub>6</sub>

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The crystal structure of Ba<sub>2</sub>CoNbO<sub>6</sub> perovskite has been studied and was found to be cubic  $Pm\bar{3}m$  with a random occupation of the Co<sup>3+</sup> and Nb<sup>5+</sup> ions at the same crystallographic site. DC susceptibility–temperature ( $\chi$ - $T$ ) curves exhibit weak ferromagnetic transitions at  $\sim 43$ – $47$  K. The transition becomes less sharp as the applied field is increased up to 50000 Oe. Finally, the transition disappears in a field of  $H = 50000$  Oe. From the logarithmic time dependence of the magnetization at 5 K, this behavior is ascribed to the formation of spin-glass or cluster-glass states, which are induced by the magnetic frustration due to the intermediate-spin (*IS*) state of Co<sup>3+</sup>. © 2000 Academic Press

## INTRODUCTION

For perovskite oxides  $ABO_3$  ( $A$ : alkaline metals, alkaline earth metals, and lanthanides;  $B$ : transition metals), it is known that the  $B$  site can accommodate two different metal ions. A general formula of such systems is given as  $A_2BB'O_6$ . Depending on the valences and relative ionic radii of all the ions involved, the  $B$  and  $B'$  ions are settled with either random or ordered arrangement as investigated for many systems so far (1–5).

One of the systems, Ba<sub>2</sub>CoNbO<sub>6</sub>, has a cubic perovskite structure with  $a = 4.06$  Å (6), where the  $B$  site accommodates the random occupation of the Co and Nb ions. The valences of the Co and Nb ions are  $3 + (3d^6)$  and  $5 + (4d^0)$ , respectively. It is well known that there are the three different electronic states for a Co<sup>3+</sup> ion in solid, denoted as the high-spin (*HS*;  $t_{2g}^4 e_g^2$ ;  $S = 2$ ), intermediate-spin (*IS*;  $t_{2g}^5 e_g^1$ ;  $S = 1$ ), and low-spin (*LS*;  $t_{2g}^6 e_g^0$ ;  $S = 0$ ) states (7, 8). These spin states change among each other depending on the radii of the  $A$ - and  $B$ -site ions and temperature, which have been elucidated from extensive studies for perovskites  $Ln_{1-x}A_xCoO_3$  ( $Ln$  = lanthanides;  $A$  = Ca, Sr, and Ba) (7, 8). The spin-state of Co<sup>3+</sup> in Ba<sub>2</sub>CoNbO<sub>6</sub> was briefly commented as the *HS* state (6).

In this work, structural and magnetic properties were investigated for Ba<sub>2</sub>CoNbO<sub>6</sub> in detail. The crystal structure at room temperature was refined by the Rietveld method. Magnetic transitions were found through DC

susceptibility–temperature ( $\chi$ - $T$ ) curves with low applied fields. The origin of the transitions is proposed on the basis of the time dependence of the magnetization.

## EXPERIMENTAL

The samples have been prepared by the solid-state reaction method (6). The starting materials were BaCO<sub>3</sub> (4N, Soekawa), Co<sub>3</sub>O<sub>4</sub> (3N, High Purity Chem. Lab.), and Nb<sub>2</sub>O<sub>5</sub> (4N, Soekawa). The initial mixtures were fired in air and O<sub>2</sub> at  $\sim 1200^\circ\text{C}$  for 10–12 h. Essentially identical results have been obtained under the two atmospheric conditions. The firing was repeated two to three times. Several samples were prepared around this temperature and were verified to show reproducible structural and magnetic properties. The oxygen contents determined from thermogravimetry are almost stoichiometric. The crystal structure was determined by powder XRD (X-ray diffraction) measurements using CuK $\alpha$  radiation (MAC Science Co., M03XHF<sup>22</sup>) with an angle ( $\theta$ ) step of  $0.04^\circ$  between  $2\theta = 10$  and  $120^\circ$ . The XRD patterns were analyzed by the Rietveld method using the program RIETAN (9).

DC magnetization measurements were performed with a SQUID magnetometer (Quantum Design MPMS-XL5). Susceptibility–temperature ( $\chi$ - $T$ ) curves were measured between 2 and 300 K in field-cooled (FC) and zero-field-cooled (ZFC) modes with an applied field ( $H$ ) up to 50000 Oe. Magnetization–applied field ( $M$ - $H$ ) isotherm curves were measured at 2 K within  $\pm 50000$  Oe. Magnetization–time ( $M$ - $t$ ) curves were measured at 5 K. The samples were maintained for two different waiting times ( $t_w$ ) 0 and 60 min following the ZFC process down to 5 K. Then the measurements were started immediately after the application of an 100 Oe field.

## RESULTS AND DISCUSSION

The XRD patterns were confirmed to consist only of the reaction products, and they were successfully refined to the cubic type structure  $Pm\bar{3}m$ . The results from the Rietveld analysis is shown in Table 1. The random occupation of the Co and Nb ions at the same crystallographic site is verified.

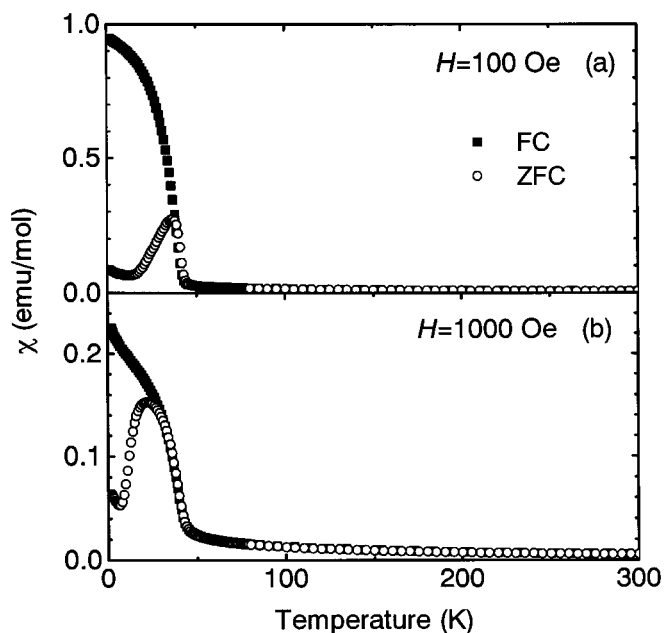
**TABLE 1**  
Crystal Structure Obtained from the Rietveld Analysis  
for Ba<sub>2</sub>CoNbO<sub>6</sub>

Atom	Occupation	x	y	z
Ba	1	0	0	0
Co	0.5	0.5	0.5	0.5
Nb	0.5	0.5	0.5	0.5
O	1	0	0.5	0.5

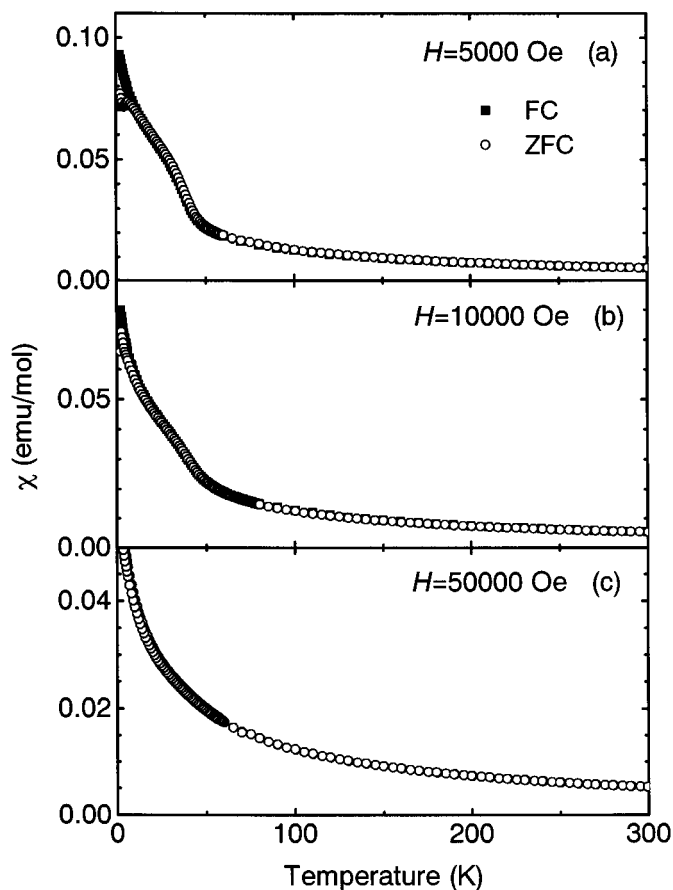
Note. Isotropic thermal parameters have been fixed to 0.3 Å<sup>2</sup>: Cubic Ba<sub>2</sub>CoNbO<sub>6</sub> (space group  $Pm\bar{3}m$ );  $a = 4.0789(1)$  Å,  $V = 67.860$  Å<sup>3</sup>;  $R_{wp} = 11.1\%$ ,  $R_1 = 5.04\%$ ,  $R_F = 2.82\%$ .

This  $Pm\bar{3}m$  structure was reported also for Ba<sub>2</sub>CoTaO<sub>6</sub> (10), containing the Ta<sup>5+</sup> ion instead of Nb<sup>5+</sup> at the same site. The lattice constant is quite close to those in Ref. (6), and also to that of Ba<sub>2</sub>CoTaO<sub>6</sub> (4.077 Å (10)) because of the identical ionic radius of Ta<sup>5+</sup> and Nb<sup>5+</sup> (11).

Figures 1a and 1b and 2a–2c show the FC and ZFC  $\chi$ - $T$  curves for Ba<sub>2</sub>CoNbO<sub>6</sub> measured with applied fields  $H = 100$  to 50000 Oe. Figure 1a shows the magnetic transition to be around 45 K. As the Nb<sup>5+</sup> ion has no 4d electrons, magnetic behaviour is ascribed only to Co<sup>3+</sup>. From inverse susceptibility-temperature ( $1/\chi$ - $T$ ) curves, dominant magnetic interactions between Co<sup>3+</sup> were found to be antiferromagnetic as noted later. The temperature derivative of the  $1/\chi$ - $T$  curves exhibited a magnetic transition temperature  $T_N = 43$ –47 K. The FC curve shows



**FIG. 1.** FC and ZFC  $\chi$ - $T$  curves for Ba<sub>2</sub>CoNbO<sub>6</sub> measured with an applied field ( $H$ ) of (a) 100 Oe and (b) 1000 Oe.



**FIG. 2.** FC and ZFC  $\chi$ - $T$  curves for Ba<sub>2</sub>CoNbO<sub>6</sub> measured with an applied field ( $H$ ) of (a) 5000 Oe, (b) 10000 Oe, and (c) 50000 Oe.

a Brillouin function-like profile below  $T_N$ , which is observed for weak ferromagnetism and canted-antiferromagnetism (12). The cusp around 20–40 K only in the ZFC curve is another property, which can be found in the case of canted-antiferromagnetism (12). The ZFC and FC curves show a large deviation below the cusp temperature  $\sim 32$ –37 K. An  $M$ - $H$  curve taken at 2 K shows a hysteresis loop, revealing the existence of magnetic order (Fig. 3).

Figure 1b shows the FC and ZFC  $\chi$ - $T$  curves for Ba<sub>2</sub>CoNbO<sub>6</sub> measured with  $H = 1000$  Oe. Although the magnetic transitions are observed around 45 K for both curves, the transition profiles are broader than those with  $H = 100$  Oe. It is also seen that the deviation between the FC and ZFC curves is fairly small compared to that in Fig. 1a, resulting in a lower cusp temperature  $\sim 21$ –25 K. These changes plausibly suggest the suppression of the magnetic order by increasing  $H$ . This was confirmed by measurements with larger applied fields as shown in Figs 2a–2c. It is evident that the magnetic transition becomes less sharp and is accompanied by a monotonous decrease of the deviation between the FC and ZFC susceptibilities as  $H$  is increased

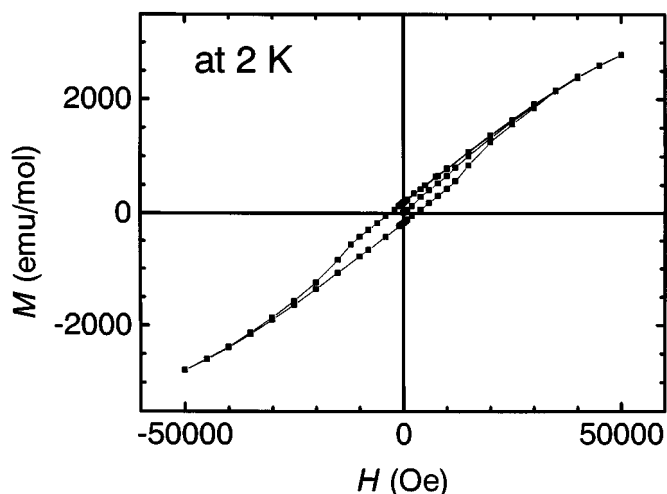


FIG. 3.  $M$ - $H$  curves for  $\text{Ba}_2\text{CoNbO}_6$  measured at 2 K.

above 5000 Oe (Fig. 2a). Both curves are almost the same in the cases of  $H = 10000$  Oe (Fig. 2b) and 50000 Oe (Fig. 2c). Finally, the magnetic order disappears at  $H = 50000$  Oe. The  $1/\chi$ - $T$  curve slightly deviates from a Curie-Weiss law below  $T_N$ , while it obeys well the CW law above  $T_N$ .

The magnetic transition in this system is very sensitive to the applied field and is completely suppressed by the  $H = 50000$  Oe field. The suppression of the magnetic transition by the field is analogous to what is observed on a solid solution titanate  $\text{La}_x\text{Gd}_{1-x}\text{TiO}_3$  (13), where the peak-like susceptibility anomaly appears around 18 K only for low applied fields (below 1000 Oe) and disappears with a field of 5000 Oe. This behaviour was assumed to originate from the formation of a spin-glass (13). Though the quantitative behaviours differ between these two systems, such a state or a similar state denoted as cluster-glass (7), seems to exist also in  $\text{Ba}_2\text{CoNbO}_6$ , as shown by the existence of the susceptibility cusps only in the ZFC curves and the deviation between the FC and ZFC susceptibilities (Fig. 1) (7). This speculation is supported also by the  $M$ - $t$  curve data at 5 K shown in Fig. 4. A logarithmic time dependence of the magnetization is observed both for  $t_w = 0$  and 60 min. As it is well known, this is a typical time dependence of magnetization in spin- and cluster-glass systems. The absence of the aging effect; i.e., the inflection of an  $M$ - $t$  curve at  $t_w$ , might be explained in terms of a cluster-glass as proposed for a magnetically frustrated perovskite systems  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  (7).

The deviation between the FC and ZFC susceptibilities, and the extremely slow relaxation discussed above can be found also in systems other than spin- and cluster-glasses, such as a superparamagnetic particle system involving no magnetic interaction between magnetic particles (14). To see whether the present behaviour is due to such a state or not,

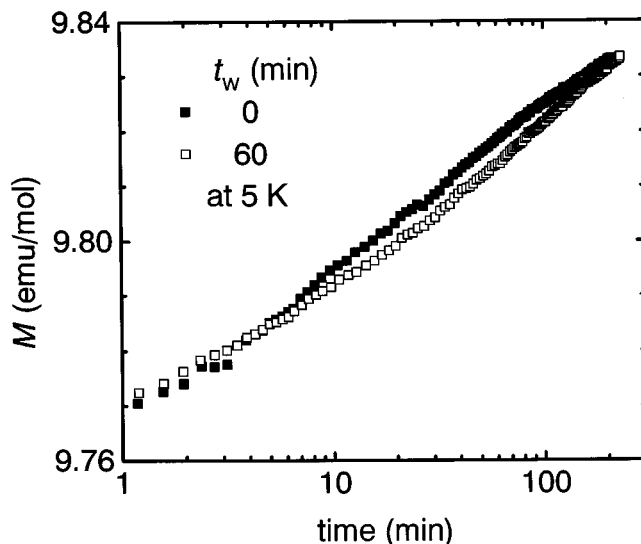


FIG. 4.  $M$ - $t$  curves for  $\text{Ba}_2\text{CoNbO}_6$  measured at 5 K with two different waiting times ( $t_w$ ) after a ZFC process ( $t_w = 0$  and 60 min).

the susceptibilities at an equilibrium state below the cusp temperature were estimated. Following Ref. (14), the magnetization ( $M$ ) was measured against time ( $t$ ) with  $H = 100$  Oe during the measurement time of  $\sim 10^5$  s, after the FC process with a few values of  $H$  (around 100 Oe) down to a few different temperatures below the cusp temperature. The equilibrium susceptibilities were estimated from the extrapolation of  $M$ - $t^{-1}$  curves to  $t^{-1} = 0$  ( $t = \infty$ ). Though there are some ambiguities because of extremely slow relaxation time, the susceptibilities showed a tendency to converge to the values quite close to the FC susceptibilities in Fig. 1a. This trend is the same as that in an  $\text{Fe}_3\text{N}$  dense sample, which was assumed to originate from the freezing of the magnetic moments of interacting particles as seen in spin-glasses (14). On the other hand, in a superparamagnetic  $\text{Fe}_3\text{N}$  system, the equilibrium susceptibilities deviate from the FC susceptibilities (14). Therefore, at present, it is expected that the phenomena observed in this work are owing to the existence of a spin-glass or a similar state noted above, i.e., cluster-glass where magnetic interactions exist between the particles (i.e., spin-clusters).

From the Curie-Weiss (CW) fit  $1/\chi = (T + \theta)/C$  for the  $1/\chi$ - $T$  curves above  $T_N$ , an effective localized moment ( $\mu$ ) of 3.79–4.09  $\mu_B/\text{Co}$  is obtained. The Weiss temperature  $\theta$  obtained is an antiferromagnetic value, 50–60 K. The value of  $\mu$  is between the spin-only values of the  $HS$  ( $S = 2$ ; 4.90  $\mu_B$ ) and  $IS$  ( $S = 1$ ; 2.83  $\mu_B$ ) states. This is different from the value reported previously, which is equal to that of the  $HS$   $\text{Co}^{3+}$  ion (6) and is almost the same as that for  $\text{Ba}_2\text{CoTaO}_6$  below 125 K (10). The present result plausibly means the coexistence of the  $IS$  and  $HS$  state, which is consistent with the

spin- or cluster-glass formation. Magnetic interactions between the *IS* Co<sup>3+</sup> ions (*t*<sub>2g</sub><sup>5</sup>*e*<sub>g</sub><sup>1</sup>) are expected to be ferromagnetic as predicted by the Hund's rule, since the Co3*d* electrons move between the neighbouring *e*<sub>g</sub> orbitals. The interactions between the *HS* Co<sup>3+</sup> ions (*t*<sub>2g</sub><sup>4</sup>*e*<sub>g</sub><sup>2</sup>) are antiferromagnetic (7). Thus the competition between ferro- and antiferromagnetic interaction leads to spin- or cluster-glass formation.

Essentially, the same results have been obtained for Ba<sub>2</sub>CoTaO<sub>6</sub> prepared in air and O<sub>2</sub> at ~1200°C, which was found to have a cubic perovskite structure *Pm* $\bar{3}$ *m* with *a* = 4.0769(1) Å. The results of the  $\chi$ -*T* curves obtained are shown in Figs. 5a-5d. The system prepared through the

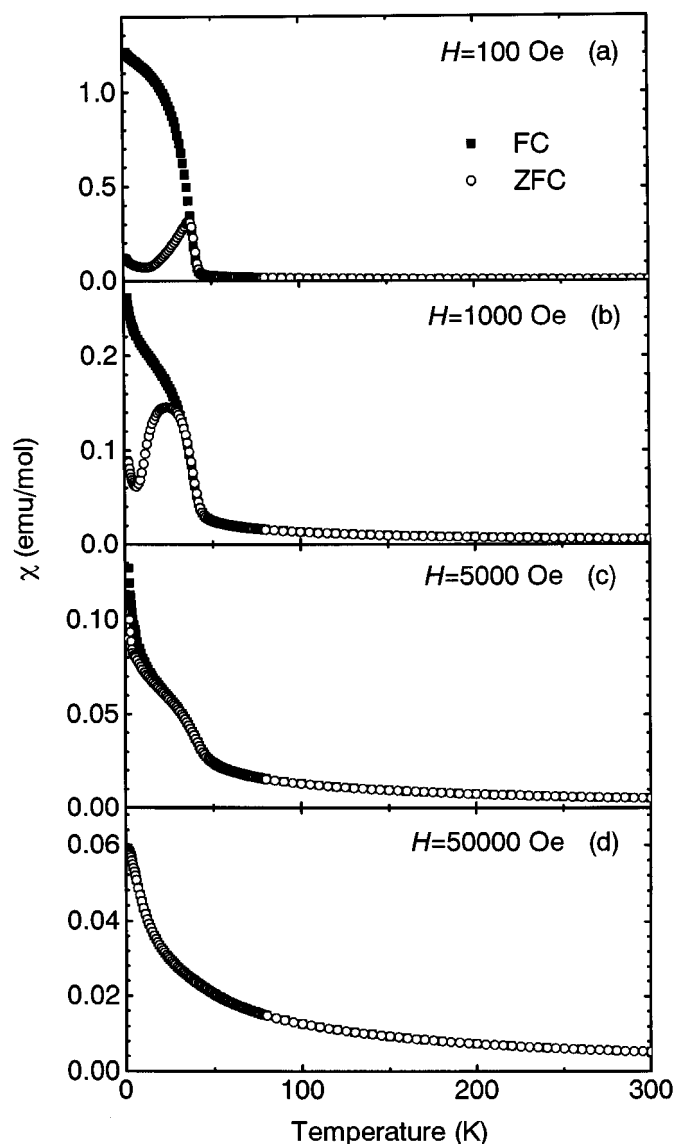


FIG. 5. FC and ZFC  $\chi$ -*T* curves for Ba<sub>2</sub>CoTaO<sub>6</sub> measured with an applied field (*H*) of (a) 100 Oe, (b) 1000 Oe, (c) 5000 Oe, and (d) 50000 Oe.

low-temperature firing process under high-pressure oxygen is a paramagnet down to 4 K (10), where the value of an applied field is not given. The transitions around 45 K and their suppression induced by the applied field are shown in these figures. The CW fit provides a localized moment of 3.57–3.86  $\mu_B$ /Co and an antiferromagnetic Weiss temperature of 42–45 K, which are similar to those found for Ba<sub>2</sub>CoNbO<sub>6</sub>. Qualitatively, the same behaviors of both *M*-*t* and *M*-*t*<sup>-1</sup> curves discussed earlier were observed as well. In spite of the oxygen deficit of ~2% in the samples estimated from thermogravimetry, these results indicate that the Co<sup>3+</sup> ions have electronic states and magnetic interaction similar to those in Ba<sub>2</sub>CoNbO<sub>6</sub>. This seems consistent since the lattice constants of both systems are very close. Investigations on other perovskite systems, such as Sr<sub>2</sub>CoMO<sub>6</sub>, are now in progress (*M*: transition metals). Detailed results will be published in the near future.

In summary, the perovskite Ba<sub>2</sub>CoNbO<sub>6</sub> has a cubic structure (*Pm* $\bar{3}$ *m*) with a random occupation of the Co<sup>3+</sup> and Nb<sup>5+</sup> ions at the same site.  $\chi$ -*T* curves exhibit weak ferromagnetic transitions at ~43–47 K. The transition becomes less sharp as the applied field is increased up to 50000 Oe. Finally, the transition disappears in a field of *H* = 50000 Oe. From the logarithmic time dependence of the magnetization at 5 K, this behaviour is ascribed to the formation of spin-glass or cluster-glass states, which is brought about by the magnetic frustration due to the *IS* Co<sup>3+</sup> ions.

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