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Magnetic Anisotropy of $Ca_3Co_2O_6$ with Ferromagnetic Ising Chains

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Magnetic properties of $Ca_3Co_2O_6$ with ferromagnetic Ising chains have been studied using oriented sample along the chain direction. From the extremely anisotropic behavior in its magnetization at low temperatures and in the temperature dependence of magnetic susceptibility, it is suggested that an octahedral Co^{3+} is nonmagnetic, whereas a trigonal prismatic Co^{3+} has a fictitious spin $S' = 1$ with large single-ion anisotropy ($D \sim -25\,\mathrm{K}, g_{//} \sim 4$). At low temperatures below 5 K, multisteps are observed in the magnetization, suggesting the existence of various magnetic structures. The pulsed magnetization measurements reveal that the response of ferromagnetic chains to the field is slow and varies as a function of temperature and $\Delta H/\Delta t$.

KEYWORDS: ferrimagnetic state, one-dimensional magnetic chain, triangular lattice, frustration, $Ca_3Co_2O_6$, Ising spin system, fictitious spin, single-spin anisotropy

§1. Introduction

Low-dimensional magnetic systems often exhibit a transition to a three-dimensional ordered state at relatively low temperatures. In the case of nearly-one-dimensional (1-D) systems such a transition is induced by the weak coupling between chains of strongly coupled spins. Quasi 1-D ABX_3 type compounds, for example, $CsCoCl_3$ and $RbFeCl_3$, were investigated extensively.[1)] There exist various magnetic ordered states according to a type of a spin of B^{2+} ion. Moreover the triangular lattice formation of the chains often induces a geometrical frustration such as a partially disordered antiferromagnetic (PDA) state which was first observed for $CsCoCl_3$.[2)]

$Ca_3Co_2O_6$[3)] with the K_4CdCl_6 type structure[4)] ($R\bar{3}c$) contains 1-D chains along the hexagonal c-axis, which form a triangular lattice in the c-plane. The infinite chains consist of alternating face sharing CoO_6 octahedra (anti-trigonal prisms, with Co1) and CoO_6 trigonal prisms (with Co2). Magnetic properties of $Ca_3Co_2O_6$ were investigated by Fjellvåg *et al.*[5)] and the present authors[6)] independently. The intrachain interaction was found to be ferromagnetic. Moreover, $Ca_3Co_2O_6$ exhibits a ferrimagnetic ordering of the ferromagnetic chains at low temperatures due to the antiferromagnetic interaction between the chains on the triangular net. As is mentioned in ref. 6, the ferrimagnetic state strongly suggests that the Co ion moment has an Ising spin character. Furthermore, we have succeeded in observing well-resolved Mössbauer hyperfine structures corresponding to the quantum levels of a $^{57}Fe^{3+}$ (^6S) ion doped in $Ca_3Co_2O_6$, indicating the very slow magnetic relaxation.[7)] This observation is attributable to the large difference in the spin character between the host (Ising) and the impurity (Heisenberg) spins.

Although the magnetic properties of $Ca_3Co_2O_6$ have been clarified to some extent, the fact that there are two different Co sites (Co1 and Co2) makes it difficult to understand the exact electronic state of each Co ion. An attempt to estimate the Co valencies based on the bond strength concept[8)] was not satisfactory, only giving the intermediate Co valence of 3.35 for Co1 and 2.25 for Co2.[3)] The moment of $3.6\,\mu_B$[6)] (or $3.9\,\mu_B$[5)]) per $Ca_3Co_2O_6$ derived from the magnetization curves is larger than $3.1\,\mu_B$ ($0.08\pm0.04\,\mu_B$ and $3.00\pm0.05\,\mu_B$ for Co1 and Co2, respectively) derived from neutron diffraction.[5)] Furthermore, the temperature dependence of magnetic susceptibility using powdered sample can not be explained without assuming large g-factor.[6)] Such situation is seen when magnetic character is highly anisotropic. Especially, in the case of d^6 (Co^{3+}, Fe^{2+}; $L = 2$, $S = 2$) and d^7 (Co^{2+}; $L = 3$, $S = 2/3$) states, an orbital angular momentum is often unquenched partially, giving a g-factor far from 2.[1,9-11)] The present study was carried out to elucidate the magnetic anisotropy of $Ca_3Co_2O_6$ using an aligned sample along the c-axis.

§2. Experimentals

The sample of $Ca_3Co_2O_6$ was prepared by a solid state reaction method from $CaCO_3$ and CoO with 99.99% purities. Powders were ground and calcined in air at 1173 K for one day. Then, the sample was reheated at 1273 K in air for a week with intermediate grindings. The powdered sample was separated into two parts, one of which was soaked into the epoxy and then the magnetic field of $H = 8\,\mathrm{T}$ was quickly applied to align the sample along the c-axis. The other was kept in the absence of magnetic field after soaked into the epoxy to form a non-oriented sample. The successful orientation along the c-axis for the former sample was confirmed by the X-ray diffraction, i.e., by the rocking curve around the index

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(006) in the hexagonal expression. We performed the magnetization measurements for both samples by means of the extraction method using a magnetometer (Quantum Design PPMS) up to 9 T at various temperatures. The temperature dependence of magnetic susceptibility χ $(=M/H)$ was measured in a static magnetic field of $H = 0.1$ T between 4 K and 300 K by using a superconducting quantum interference device magnetometer (Quantum Design MPMS). To investigate the response of the ferromagnetic chain (or Co spins) to the field sweep, the pulsed field magnetization measurements were performed as a function of T and $\Delta H/\Delta t$ by an induction method with well balanced pick-up coils. The duration time of the pulsed magnetic field was 12 ms.

§3. Results and Discussion

In the inset of Fig. 1, we show the temperature dependence of magnetic susceptibilities of $Ca_3Co_2O_6$ along the c-axis, $\chi_{//}$, perpendicular to the same axis, $\chi_{\perp}$, and non-oriented (random), χ_r. It is obvious that $\chi_{//}$ is much larger than $\chi_{\perp}$, indicating the extremely large anisotropy along the c-axis. The parallel susceptibilities $\chi_{//}$ obey the Curie-Weiss law at high temperatures above 150 K (region 2). Below 150 K (region 1) the deviation from the Curie-Weiss law becomes appreciable. The representative magnetization curves in static fields up to 9 T are shown in Fig. 2, which also implies the uniaxial anisotropy. A clear plateau of 1/3 of the saturation moment of 2.2×10^4 emu/mol (corresponding to $4\mu_B/Ca_3Co_2O_6$) is observed in the M-H curve at 12 K, indicating the ferrimagnetic state where the ferromagnetic chains order antiferromagnetically at the ratio of 2 to 1 on the triangular lattice. Though the $M_{\perp}$-H curve at 12 K also have a plateau, it is probably not the intrinsic property of $Ca_3Co_2O_6$ but due to the imperfect alignment. It is noted that M_r is somewhat smaller than the magnetization measured in the case of powdered sample.[6] This indicates that powder of $Ca_3Co_2O_6$ tends to orient with increasing H. The divergence in magnetization data between Aasland *et al.* and the present authors should be attributed to the difference of the mobility of the powder.[5,6]

Now let us discuss the electronic states of two different Co sites. The moment of $4\mu_B$ per $Ca_3Co_2O_6$ is evaluated from the magnetization measured using the aligned sample along the c-axis. On the other hand, the neutron diffraction suggests $0.08\,\mu_B$ and $3.00\,\mu_B$ for Co1 and Co2, respectively.[5] It is reasonably conjectured from these facts that Co1 is nonmagnetic while Co2 is magnetic having an Ising-like spin moment of about $4\mu_B$. This strongly gives an implication that both Co1 and Co2 ion are trivalent, i.e., d^6 state. The large energy level split between the dε and dγ orbitals should give the low spin configuration at Co1. It should be mentioned that the larger crystalline field effect is expected for the octahedral Co1 than for the trigonal prismatic Co2, thus leading to different spin configurations.[12]

The extremely anisotropic magnetic behavior of $Ca_3Co_2O_6$ can be interpreted using effective spin with $S' = 1$ for Co^{3+} (Co2), following the treatment shown by Lines[9] and Oguch.[11] Figure 3 shows the schematic

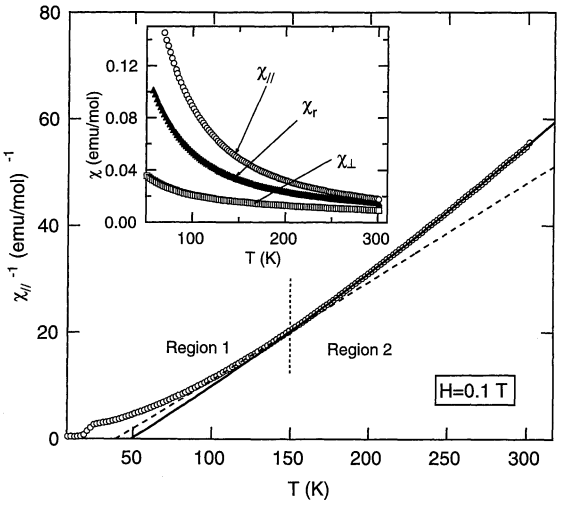

Fig. 1. Reciprocal molar susceptibility $\chi_{//}^{-1}$ of $Ca_3Co_2O_6$ as a function of temperature. The broken and solid curves indicate the caluculated reciprocal susceptibilities using eqs. (1) and (2) for region 1 and region 2, respectively. Inset: molar susceptibilities, $\chi_{//}$, $\chi_{\perp}$ and χ_r as a function of temperature.

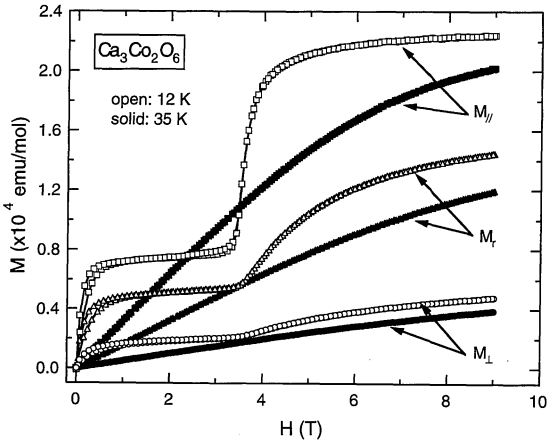

Fig. 2. Magnetization curves of $Ca_3Co_2O_6$ in static magnetic fields for $0\,T \leq H \leq 9\,T$ at 12 K (open) and 35 K (solid). Squares denote $M_{//}$, circles $M_{\perp}$, and triangles M_r.

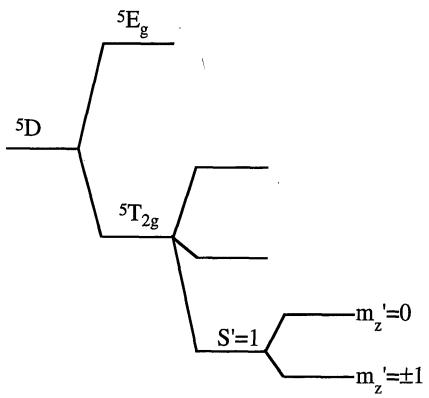

Fig. 3. Schematic energy level diagram of a trigonal prismatic Co^{3+} in $Ca_3Co_2O_6$.

illustration of the energy level structure with uniaxial anisotropy in the absence of exchange interaction and external magnetic field. In the weak-field-coupling scheme the free ion ground state of a Co^{3+} ion, i.e., ^5D ($L = 2, S = 2$), is split by the cubic part of the crystalline field into an upper orbital doublet (^5E_g) and a lower orbital triplet ($^5T_{2g}$). Considering only T_{2g}, we can define a fictitious orbital angular momentum $L' = 1$ from the structural equivalence of the T_{2g} and P symmetry groups. Since $\lambda < 0$ (where λ is the spin-orbit coupling parameter of a free Co^{3+} ion), a fictitious spin $S' = 1$ is a good quantum number if a single-ion anisotropic energy of the form DS_z^2 caused by the interaction with the crystalline field is large compared with the exchange interaction J. If D is negative, the single-ion anisotropy leads locally to a splitting of the triplet state into a doublet ground state with $m'_z = \pm 1$ and a singlet ($m'_z = 0$) excited state (where m'_z is the z component of S') as shown in Fig. 3.

In the following analysis, we assume that the excited levels with $S' = 2$, 3 are neglected. The fictitious spin $S' = 1$ can be used for the lowest three levels in the temperature region 1 in Fig. 1. An appreciable contribution to the susceptibility from the singlet excited state may be found in the temperature region 2. The parallel susceptibility was calculated for $S' = 1$ following Achiwa.[1] When $J_{/\!/} < kT$, the magnetic susceptibility along the easy axis can be expressed as

$$\chi_{/\!/} = \frac{2Ng_{/\!/}^2\mu_B^2}{kT\{\exp(D/kT) + 2\} - 8J_{/\!/}}, \tag{1}$$

and at high temperature limit this gives

$$\chi_{/\!/} = \frac{2Ng_{/\!/}^2\mu_B^2}{3kT + D - 8J_{/\!/}}, \tag{2}$$

where only the nearest neighbor intrachain exchange interaction $J_{/\!/}$ is taken into consideration. The observed $\chi_{/\!/}$ in the region 2 could be fitted best to the calculated value using eq. (2) with $(D - 8J_{/\!/})/k = -145.8\,\mathrm{K}$ and $g_{/\!/} = 4.53$ accompanied with a constant susceptibility $\chi_0 = -3.0 \times 10^{-3}$ emu/mol as shown in Fig. 1. The large value of $g_{/\!/} = 4.5$ is due to the large single-ion anisotropy. Similar value of $g_{/\!/} = 4.0$ can be evaluated from the saturation moment of $4\mu_B$ by assuming $S' = 1$. The fit of $\chi_{/\!/}$ in the region 1 to eq. (1) was not satisfactory due to the simplicity of the model. But together with the above result, we can roughly estimate the parameters as $D/k = -25\,\mathrm{K}$, $J_{/\!/}/k = 15\,\mathrm{K}$. The obtained negative sign of D is in accordance with the assumption that the ground state is a doublet with $m'_z = \pm 1$. The obtained positive sign of $J_{/\!/}$ indicates the ferromagnetic intrachain interaction. The magnitudes of D and $J_{/\!/}$ are comparable with $D/k = 18.4\,\mathrm{K}$ and $J_{/\!/}/k = -11.5\,\mathrm{K}$ for $RbFeCl_3$,[1] which is widely known as an ideal triangular XY-like antiferromagnet with $S' = 1$ (in the case of $D > 0$, the triplet $S' = 1$ state split into the singlet ground state and the doublet excited state). The perpendicular terms, $g_\perp$ and $J_\perp$ can not be determined because, as mentioned above, intrinsic $\chi_\perp$ is disturbed by the imperfect sample orientation along the easy axis. The magnetic properties of Sr_3NiIrO_6 isostructural with $Ca_3Co_2O_6$ were also investigated in terms of the high single-ion anisotropy, and fairly large value of $D = 90.2\,\mathrm{K}$ was obtained for Ni^{2+} ions ($S = 1$) at trigonal prism site from the magnetic susceptibility.[13] It is noted that the sign of D is opposite to the case of $Ca_3Co_2O_6$.

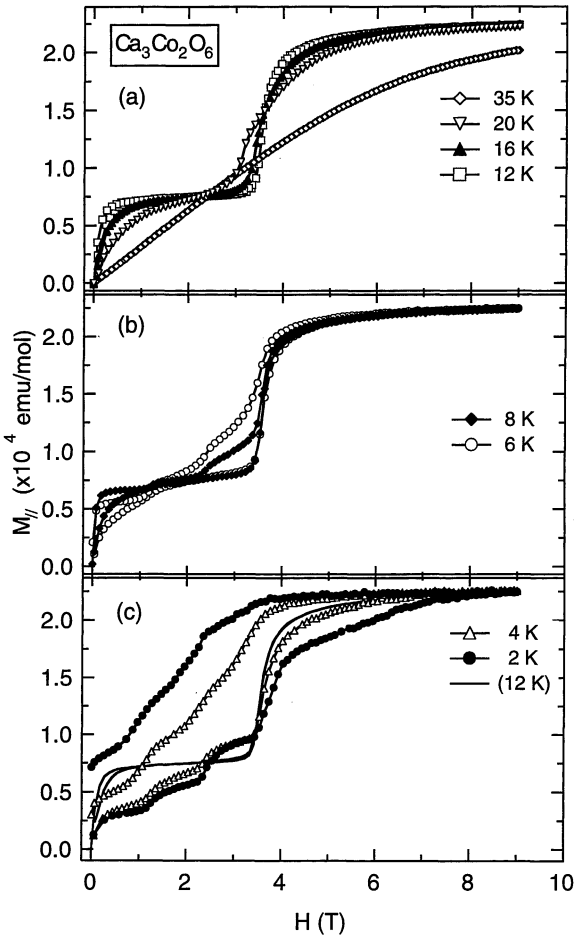

Fig. 4. $M_{/\!/}$ vs. H curves measured in static fields for $0\,\mathrm{T} \leq H \leq 9\,\mathrm{T}$ at 35 K, 20 K, 16 K and 12 K (a), 8 K and 6 K (b), and 4 K and 2 K (c). For comparison, the magnetization curve at 12 K is also shown by the solid curve in (c).

Next, we turn our attention to the low temperature magnetic properties. Parallel magnetization curves at various temperatures are shown in Fig. 4. There is almost no hysteresis for the M-H curves above 10 K (Fig. 4(a)), whereas below 10 K the hysteresis is appreciable (Figs. 4(b) and 4(c)). As for the measurements at 2 K and 4 K, with increasing magnetic field, there appears three plateaus (except for the saturated one) corresponding to about 3×10^3 emu/mol, 6×10^3 emu/mol and 9×10^3 emu/mol, which was not found in the previous study because the data were taken at every 0.5 T.[6] It is likely that many complicated magnetic structures exist in temperature and magnetic field domains. At low temperatures, the small exchange interaction such as 3rd and 4th nearest neighbor J would become important, thus giving the complicated magnetic structures. Takagi and Mekata[14] proposed the candidates of the magnetic structures of Ising spins on a triangular lattice. The lowest plateau with about 1/5 of the full moment may cor-

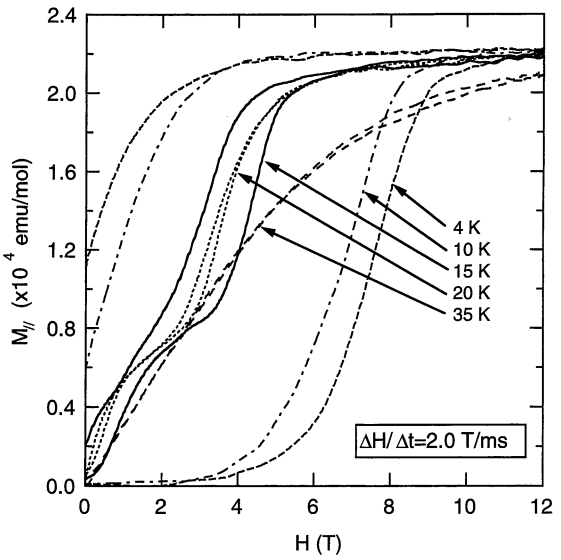

Fig. 5. $M_{//}$ vs. H curves measured under pulsed magnetic fileds with $\Delta H/\Delta t = 2.0\,\mathrm{T/ms}$ at 35 K, 20 K, 15 K, 10 K and 4 K.

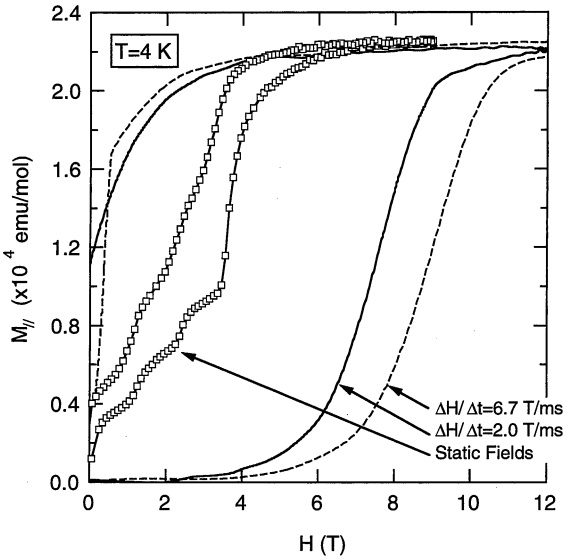

Fig. 6. $M_{//}$ vs. H curves at 4 K with the field sweeping rates of $\Delta H/\Delta t = 6.7$, 2.0 and 0 T/ms.

respond to a 5-sublattice structure,[14] where 3/5 of the up ferromagnetic-chains and the rest 2/5 of the down ferromagnetic-chains order antiferromagnetically. It is noted that the plateaus at 2 K is clearer than those at 4 K. This may be because the thermal fluctuation easily disturbs the magnetic orderings. The ground state in the absence of magnetic field is of great interest. At the moment, the authors suppose that the ground state should be like the one where many stable magnetic structures compete with each other.

From the Arrott plots for the magnetization data, the PDA state was suggested for $10\,\mathrm{K}(=T_{c2})<T<25\,\mathrm{K}(=T_{c1})$,[6] where 2/3 of the ferromagnetic chains order antiferromagnetically with each other and the remaining 1/3 are left incoherent with the other chains. The Arrott plots, however, are based upon a mean-field theory (the Landau expansion of free energy). It is uncertain whether or not the Arrott plots are applicable to the present material having a uniaxial anisotropy.

Finally the parallel magnetizations measured using pulsed fields with the rates of $\Delta H/\Delta t = 2.0\,\mathrm{T/ms}$ are shown in Fig. 5. The M-H curve at 35 K ($>T_{c1}$) almost coincides with that measured in static magnetic fields at the same temperature. The magnetizations using pulsed fields at lower temperatures are different from the data measured with static fields. Especially there is large hysteresis in the M-H curve for $T \leq 10\,\mathrm{K}$. These results indicate that the ferromagnetic chains (or Ising spins of Co2 ions) respond to an external magnetic fields very slowly at the order of 10^{-3} s. In Figs. 6 and 7, we show the magnetization curves measured with various field sweeping rates at 4 K and 15 K, respectively. Clearly the response of the ferromagnetic chains to the external field gets slower with increasing $\Delta H/\Delta t$. The relatively slow propagation of the domain walls along the ferromagnetic chains is considered as a mechanism of the chain reversal.

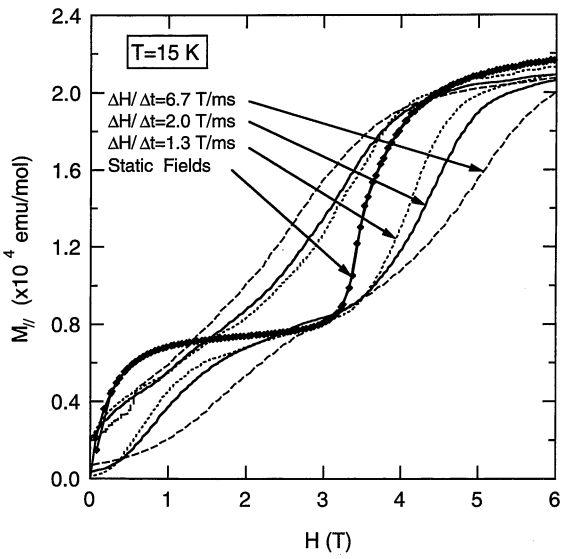

Fig. 7. $M_{//}$ vs. H curves at 15 K with the field sweeping rates of $\Delta H/\Delta t = 6.7$, 2.0, 1.3 and 0 T/ms.

§4. Conclusions

In summary, we have investigated the magnetic properties of $Ca_3Co_2O_6$ using an aligned sample along the c-axis. As expected from the ferrimagnetic structure indicating the Co ions being Ising-like spins, an extremely anisotropic behavior in the M-H and χ-T data was observed. The moment per $Ca_3Co_2O_6$ was determined to be $4.0\,\mu_B$ from the parallel magnetizations. It is suggested that the Co1 ion is nonmagnetic, while the Co2 ion has a fictitious spin $S' = 1$ with large single-ion anisotropy ($D \sim -25\,\mathrm{K}, g_{//} \sim 4$). For $T \leq 4\,\mathrm{K}$, the multimetamagnetic transitions were observed. More detailed neutron diffraction study is needed to clarify the magnetic structures. The ferromagnetic chains shows a slow response to the magnetic field.

1) N. Achiwa: J. Phys. Soc. Jpn. **27** (1969) 561.
2) M. Mekata: J. Phys. Soc. Jpn. **42** (1977) 76.
3) H. Fjellvåg, E. Gulbrandsen, S. Aasland, A. Olsen and B. C. Haucack: J. Solid State Chem. **124** (1996) 190.
4) G. Bergerhoff and O. Schmitz-Dumott: Z. Anorg. Allg. Chem. **284** (1956) 10.
5) S. Aasland, H. Fjellvåg and B. Hauback: Solid State Commun. **101** (1997) 187.
6) H. Kageyama, K. Yoshimura, K. Kosuge, H. Mitamura and T. Goto: J. Phys. Soc. Jpn. **66** (1997) 1607.
7) H. Kageyama, S. Kawasaki, K. Mibu, M. Takano, K. Yoshimura and K. Kosuge: Phys. Rev. Lett. **79** (1997) 3258.
8) N. E. Base and M. O'Keeffe: Acta Crystallogr. Sec. B **47** (1991) 192.
9) M. E. Lines: Phys. Rev. **131** (1963) 546.
10) N. Suzuki: J. Phys. Soc. Jpn. **50** (1981) 2931.
11) T. Oguchi: J. Phys. Soc. Jpn. **20** (1965) 2236.
12) K. F. Purcell and J. C. Kots: Inorg. Chem. **9&10** (Holt-Saunders International Editions, Japan, 1985).
13) T. N. Nguyen, D. M. Giaquinta and H.-C. zur Loye: Chem. Mater. **6** (1969) 1642.
14) T. Takagi and M. Mekata: J. Phys. Soc. Jpn. **64** (1995) 4609.