Intermediate Phase IV in Structural Phase Transitions of TlCoCl₃

Yoichi NISHIWAKI*, Akira OOSAWA¹, Tetsuya KATO², Takumi HASEGAWA³, Haruhiko KUROE¹, and Kazuhisa KAKURAI⁴

1 Department of Physics, Tokyo Women’s Medical University, Shinjuku-ku, Tokyo 162-8666
2 Department of Physics, Sophia University, Chiyoda-ku, Tokyo 102-8554
3 Graduate School of Integrated Arts & Sciences, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8521
4 Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195

(Received August 15, 2008)

The structural changes of TlCoCl₃ around phase IV (68 K < T < 75 K) were studied by single-crystal neutron diffraction measurement. The present investigation revealed that a small but definite Bragg peak at (a/2 a/2 2) appeared only in phase IV. A precursor phenomenon of the phase V (T < 68 K) structure in the phase IV temperatures was also identified as the coexistence of a slightly broadened (a/2 a/2 2) Bragg peak. We confirmed that intermediate phase IV is a stable, nontransient, single phase with 2√3a x 2√3a x c unit cells. A possible sequence of structural phase transitions was proposed.

KEYWORDS: TlCoCl₃, triangular lattice, neutron diffraction, structural phase transition.

1. Introduction

Among magnetic compounds with simple component ions, those with a CsNiCl₃-type structure¹⁻³ (space group hexagonal P6₃/mmc) exhibit strong one-dimensional magnetic correlations.⁴,⁵ For those with the ABX₃ chemical formula, where A, B, and X are alkali, 3-d, and halogen ions, respectively, the linear-chain -BX₃- substructure along the c-axis is magnetically well separated by intervening A ions. From the higher-temperature phase with this structure, a group of compounds show successive structural phase transitions. We call these compounds members of the KNiCl₃ family.⁶⁻⁸ Lattice distortions of KNiCl₃ family compounds are characterized by -BX₃- chain shifts along the c-axis,⁹,¹⁰ Representative of these compounds are KNiCl₃¹¹⁻¹⁷ and RbMgBr₃,¹⁸⁻²² whose room-temperature (RT) structure has tripled (√3a x √3a x c; a and c are lattice constants of the prototype CsNiCl₃-structure) unit cells with chain shifts along the c-axis in an up-up-down manner, as shown in Fig. 1(a). This phase is called phase III and the structure, sometimes called the ‘RT-KNiCl₃-structure’, was reported to take symmetries of the space group P6₃cm. However, it was not excluded by diffraction analysis¹¹,¹² that the phase III structure may be another one with P3c1 symmetry characterized by up-down type chain shifts, as shown in Fig. 1(b).²³⁻²⁵ Interestingly, the lowest-temperature (phase V) structure is an orthorhombic (space group Pbcn) quadruplicated (2√3a x 2√3a x c) one with up-up-down-down type chain shifts, as shown in Fig. 1(c).²⁶ The same sequence of successive structural phase transitions were hitherto observed in TlCoCl₃,²⁶ TlFeCl₃,²⁷,²⁸ and RbMgBr₃.²⁹ The characteristics of higher-temperature phases I and II are not so simple that one should refer to the previous studies.¹³,¹⁶,¹⁹

The reason the -BX₃-chain substructure is preserved and only the reassemblage occurs at low-temperature structural change is not clarified. It must be related to ferroelectricity, observed as the small spontaneous polarization along the chain direction in phase III with a unique temperature dependence, and also in phase IV with a notable enhancement.¹⁵,¹⁹ The polarization, however, disappeared in phase V where chain shifts are needed for complete reassembly. Among the above crystals, TlCoCl₃ is suitable for the investigation of the structural change among phases III, IV, and V avoiding thermal fluctuation, because the transition points T₃=75 K (III→IV) and T₄=68 K (IV→V) are the lowest.

In our previous neutron scattering study of TlCoCl₃,³⁰ (we call it Paper I), mainly concerned with TlCoCl₃ magnetism, we confirmed the phase III and phase V structures of this crystal. In the temperature dependence of single-crystal Bragg peak height (shown as Fig. 6(b) in Paper I), the alternation between the peaks of phases III and V were represented around phase IV (T₄<T< T₃). It was quite unusual that both the Bragg peaks for phase V at (a/2 a/2 2) and for phase III at (a/2 a/2 2) coexist at phase IV temperatures, even though the lower phase transition at T₄ is of the first order. It could become uncertain that the ‘phase IV’ would be unstable or the data around those temperatures could be obtained only transiently. In this study, we performed single-crystal neutron scattering, specifically focused at these temperatures and found a Bragg peak at (a/2 a/2 2) that appeared only in phase IV. This indicates that the intermediate phase IV is a stable, nontransient phase.

2. Experimental Procedure

The method of preparing single crystals of TlCoCl₃ is stated in our previous report.²⁶ The neutron scattering for single-crystal measurement was performed with the triple-axis spectrometer TAS2 installed at JRR-3M of the Japan Atomic Energy Agency (JAEA), Tokai. A pyrolytic graphite (0 0 2) reflection was used as
the monochromator and analyzer. Higher-order neutrons were removed using a pyrolytic graphite filter set in front of and behind the sample. Neutron energy was fixed at 14.7 meV (k = 2.66 rad/Å). Horizontal collimations were chosen to be 14′ - 80′ - 80′ - 80′. The sample, about 0.5 cm³ in volume, was mounted in a 10 K refrigerator and the temperature of the sample was measured with a calibrated silicon diode thermometer. The experimental results are indexed on the prototype CsNiCl₃-type lattice, the same as in our previous study. The [110] axis was arranged vertically to measure scattering intensity in the (h h l) zone. The lattice constants at T = 60 K were a = 6.91 Å and c = 5.98 Å.

3. Results

As shown in Paper I, superlattice reflections that involve structural phase transitions are extinct in the (h h l) zone owing to the existence of a set of symmetry operations of c glide planes, one of which transforms (x y z) into (y x z + 1/2). This is a common nature of all structural phases of the KNiCl₃ family compounds. This is confirmed again in this study, so we start to describe the results of the q-scan profiles of (h h 2). The representative profiles from h = 0.15 to 0.36 at 86.4 K (phase III), 71.7 K (phase IV), and 60.0 K (phase V) are shown in Fig. 2(a). In phase III, Bragg reflections were measured at 1/3 and 2/3, the latter of which appeared in a wide q-scan measurement. In phase V, in-plane reflections at h = 1/4 and 3/4 were observed, in addition to off-plane reflections at h = 3/8 and 5/8 that were detected owing to the coarse vertical resolution. Very small Bragg reflections at h = 1/8 were observed in phase V. These results were consistent with those in Paper I. In phase IV, in addition to the peaks observed in phases III and V, reflections at h = 1/6 and 5/6 were observed. The (1/6 1/6 2) peak was observed only at temperatures between T_{st3} and T_{st4}, as shown in Fig. 2(b). The full width at half maximum (FWHM) of this peak was constant in phase IV, at approximately 7.0×10⁻³ Å⁻¹ with a resolution limit. An asymmetric broad background was also observed with increasing intensity with increasing temperature.

The temperature dependence of (1/3 1/3 2) peak height is shown in Fig. 3(a). The heating and cooling rates were 1.8 and 0.7 deg/min, respectively. The thermal hysteresis around the first-order phase transition at T_{st4} was clearly indicated. Note that spontaneous polarization had a quite similar temperature dependence to the present results. Now, it is unlikely that phase IV could be a crossover between phases III and V, which is stated in Paper I. Thus, the present results exhibited phase IV as a single phase that is characterized by the (1/6 1/6 2) peak.

The temperature dependences of peak height at (1/4 1/4 2) and (1/4 1/4 2) are shown in Fig. 6(b) in Paper I. Apparently, the ‘phase V peak’ at (1/4 1/4 2) survived at temperatures up to approximately 90 K, namely in phase IV and even in phase III, although the ‘phase III peak’ at (4/6 4/6 2) vanished in phase V (below T_{st4}). In this study, we evaluated the temperature dependence of the FWHM of the peaks. The results are shown in Fig. 3(b). In phase IV, the FWHM of the phase III peak was the resolution limit, although that of the phase V peak was definitely broadened with increasing temperature. Thus, a precursor phenomenon or an aftereffect with a quite strong short-range correlation with an (h k)= (4/6 4/6) periodicity was suggested to remain above T_{st4} and even above T_{st3}.

4. Discussion

In this study, we found the (1/6 1/6 2) peak appeared in phase IV. The scattering intensities of the (1/3 1/3 2) and (1/3 1/3 2) peaks are similar to the results in Paper I. The maximum intensity of the (1/3 1/3 2) peak is approximately one-tenth those of the (1/3 1/3 2) and (1/3 1/3 2) peaks. The
structural model in phase IV should be one in which a small periodic modulation with a wave number \((h, k) = (\frac{1}{6}, \frac{1}{6})\) is added to the phase-III structure.

The structure of phase III was described as the freezing of the vibrational \(K_4(1, -1)\) mode of the prototype CsNiCl\(_3\) (\(P6_3/mmc\)) structure\(^{31, 32}\), where \((1, -1)\) indicates the antiphase combination of two order parameters in the \(K_4\) mode. Here, note that the \(P3c1\) symmetry is obtained from their \((1, 1)\) combination, which is the alternative symmetry for phase III, or that the \(P3c1\) symmetry from other combinations. For both phases IV and V, such modes should be described as \(T_2\) modes, because the wave vector is on the \(T\) line (connected between the \(\Gamma\) and \(K\) points) and the ionic displacements along the \(c\)-axis must be the same for all chains. The specific displacements of \(T_2\) modes and their space group symmetry will be listed in the further work. Compatibility relations for symmetry modes of \(P6_3/mmc\) show that both \(K_4\) and \(T_2\) modes are compatible with the \(A_{2u}\) mode, as listed in Tables XIV-XVII in the paper by Mañes et al.\(^{32}\). Here, we picked the \(B\) ion displacements along the \(c\)-axis, which describe nondeformed chain shifts, as shown in Table I. Accordingly, in both phase IV and phase V lattice distortions, the \(A_{2u}\) mode can coexist as a consisting amplitude. Nevertheless, a zero amplitude for the \(A_{2u}\) mode is expected for the phase-V structure because of the centrosymmetric combination of several order parameters in the \(T_2\) mode in phase V. In phase IV, a hexagonal combination of them should be assumed.

Although the phase IV symmetry was not uniquely determined as \(P3c1\), it is one of the most plausible candidates for the following reasons. Here, we pay attention on both possibilities of symmetry for the phase III structure \((a^{III} \times a^{III} \times c\) unit cells\) as \(P6_3cm\) and \(P3c1\). Experimental results indicate the phase transition III→
IV at $T_{a4}$ should be continuous so that the phase IV symmetry should be a uniaxial, hexagonal or rhombohedral subgroup of phase III symmetry. According to the International Tables for Crystallography (ITC),\textsuperscript{33} both $P6_3cm$ and $P3c1$ symmetries are themselves the maximal isomorphic subgroups of index 4 ($d^{IV} = 2d^{III}$).

As long as the translational symmetry of phase IV exists, $P6_3cm$ and $P3c1$ can be candidates; however, the spontaneous polarization $P_s$ of phase IV indicates directly that the centrosymmetric $P3c1$ is not suitable. Thus, the candidate symmetry was restricted within $P6_3cm$ itself and the subgroups of $P6_3cm$ and $P3c1$. The maximal non-isomorphic subgroups of $P6_3cm$ are $P6_3$, $P3c1$ and $P31m$, and those of $P3c1$ are $P321$, $P3$ and $P3c1$, as shown in ITC.\textsuperscript{33} Among these five subgroups, only $P3c1$ is suited for the observed extinction rules for the existence of a glide plane symmetry. Consequently, three kinds of phase transition sequence around phase IV can be proposed, as shown in Table II.

We assume that the sequence $P3c1$ (phase III) $\rightarrow$ $P3c1$ (IV) $\rightarrow$ $Pbca$ (V) is the most plausible because the spontaneous polarization is quite small in phase III but relatively large in phase IV.\textsuperscript{26} If the phase III structure is $P6_3cm$, it can hardly explain why the spontaneous polarization in phase IV is much larger than that in phase III. It might be that the spontaneous polarization is zero in phase III ($P3c1$) and only appears in phase IV ($P3c1$). The quite small polarization in phase III may be caused by phase-shift domains or twinning in the $P3c1$ structure. The regions of up-up-down, up-up-down-down and up-0-down-0 type chain shifts tend to appear at phase boundaries when the phase transition occurs from $P6_3/mmc$ to $P3c1$.\textsuperscript{34} The up-up-down region at the boundaries can induce the small polarization. In addition, another up-up-down-down region on the boundaries might explain the present results showing the precursor or short-range phase V ordering even above $T_{a4}$. Therefore, a structural reinvestigation of phase III using a four-axis spectrometer or some other techniques and the determination of the phase IV structure in further works are needed to confirm this $P3c1$-structure scenario for successive structural phase transitions. The phase transition sequence of $\text{TiCoCl}_3$ should be common to those of $\text{KNiCl}_3$, $\text{RbMnBr}_3$ and $\text{TIFeCl}_3$.

In conclusion, we performed single-crystal neutron diffraction measurement in $\text{TiCoCl}_3$. Phase IV was shown as a single phase with $2\sqrt{3}a \times 2\sqrt{3}a \times c$ unit cells, because a Bragg peak at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ appeared only in phase IV. The temperature dependence of this peak is quite similar to that of spontaneous polarization. We confirmed that phase III, IV and V structures are characterized by the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$, $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ peaks, respectively. A possible structural phase transition sequence was proposed.

### Acknowledgment

The authors would like to express their sincere thanks to K. Iio, T. Sekine and T. Asahi for useful discussions.

### Table II. Possible phase transition sequences around phase IV.

| structural phase unit cell mode | III $\sqrt{3} \times \sqrt{3}$ | IV $2\sqrt{3} \times 2\sqrt{3}$ | V $2\sqrt{3} \times \sqrt{3}$ |
|---------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $K_1 (\frac{1}{2})$            | $T_2 (\frac{1}{2})$           | $T_2 (\frac{1}{2})$           |
| (1) $P6_3cm$                   | $P6_3cm$                      | $Pbca$                        |
| (2) $P6_3cm$                   | $P3c1$                        | $Pbca$                        |
| (3) $P3c1$                     | $P3c1$                        | $Pbca$                        |

1. J. B. Goodenough and J. A. Kafalas: J. Solid State Chem. 1 (1969) 103.
2. J. M. Longo and J. A. Kafalas: J. Solid State Chem. 3 (1971) 429.
3. M. L. Pummer, Kevin Hood, and A. Caille: J. Phys. C: Solid State Phys. 21 (1988) 4189.
4. N. Achiwa: J. Phys. Soc. Jpn. 27 (1969) 561.
5. M. F. Collins and A. Petrenko: Can. J. Phys. 75 (1997) 605.
6. K. Morishita, N. Nakano, T. Kato, K. Iio, and T. Mitsu: Ferroelectrics 217 (1998) 207.
7. T. Mitsu, M. Nasui, K. Morishita, T. Kato, and K. Iio: Ferroelectrics 238 (2000) 97.
8. K. Yamanaka, Y. Nishiwaki, K. Iio, T. Mitsu, T. Tojo, and T. Atake: J. Thermal Analysis and Calorimetry 70 (2002) 371.
9. Z. W. Hendriksen and W. J. A. Maaskant: Physica B 233 (1997) 136.
10. T. Hasegawa and K. Iio: J. Korean Phys. Soc. 46 (2005) 59.
11. D. Visser, G. C. Verschoor, and D. J. W. Ijdo: Acta Crystallogr. B 36 (1980) 28.
12. D. Visser and A. Prodan: Phys. Status Solidi A 58 (1980) 481.
13. D. Visser, R. G. Delaflane, and W. J. A. Maaskant: Physica B276-278 (2000) 300.
14. O. A. Petrenko, M. F. Collins, C. V. Stager, B. F. Collier, and Z. Tunk: J. Appl. Phys. 79 (1996) 6614.
15. O. A. Petrenko, M. A. Lumsden, M. D. Lumsden, and M. F. Collins: J. Phys.: Condens. Matter 8 (1996) 10899.
16. K. Machida, T. Mitsu, T. Kato, and K. Iio: Solid State Commun. 91 (1994) 17.
17. K. Machida, T. Kato, P. S. Chao, and K. Iio: J. Phys. Soc. Jpn. 66 (1997) 3283.
18. T. Kato, K. Iio, T. Hoshino, T. Mitsu, and H. Tanaka: J. Phys. Soc. Jpn. 61 (1992) 275.
19. T. Kato, K. Machida, T. Ishii, K. Iio, and T. Mitsu: Phys. Rev. B50 (1994) 13039.
20. T. Kato: J. Phys. Soc. Jpn. 71 (2002) 300.
21. L. H. Heller, M. F. Collins, Y. S. Yang, and B. Collier: Phys. Rev. B49 (1994) 1104.
22. H. Fink and H.-J. Seifert: Acta Crystallogr. B38 (1982) 912.
23. A. Hauser, U. Falk, P. Fischer, and H. U. Güdel: Journal of Solid State Chemistry 56 (1985) 343.
24. H.-J. Seifert and J. Wäsle-NIelen: Rev. Chim. Minère 14 (1977) 503.
25. P. L. Kirklin and G. L. McPerson: J. Phys. C: Solid State Phys. 8 (1985) 343.
26. Y. Nishiwaki, K. Iio, and T. Mitsu: J. Phys. Soc. Jpn. 72 (2003) 2608.
27. K. Yamanaka and T. Kato: J. Phys. Soc. Jpn. 71 (2002) 1757.
28. A. Zodkevitz and J. Makovsky: Israel J. Chem. 8 (1970) 755.
29. K. Gesi: Ferroelectrics 301 (2004) 133.
30. (Paper I) Y. Nishiwaki, T. Kato, Y. Oohara, A. Oosawa, N. Todoroki, N. Igawa, Y. Ishii, and K. Iio: J. Phys. Soc. Jpn. 75 (2006) 034707.
31. J. M. Pérez-Mato, J. L. Mañes, M. J. Tello, and F. J. Zúñiga: J. Phys. C: Solid State Phys. 14 (1981) 1121.
32. J. L. Mañes, M. J. Tello, and J. M. Pérez-Mato: Phys. Rev. B26 (1982) 250. Their atomic notation $A$, $B$, $X$, should be read as $B$, $A$, $X$, respectively, except for Fig. 1.
33. International Tables for Crystallography, ed. T. Hahn (Kluwer Academic Publishers, City of Publication, 1992) Vol. A.
34. T. Hasegawa: Dr. Thesis, Department of Physics, Tokyo Institute of Technology, Tokyo, 2005.