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ARTICLES

Multicritical point in structurally incommensurate $[N(CH_3)_4]_2CuCl_4$ under pressure

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The x-ray-diffraction experiment of $[N(CH_3)_4]_2CuCl_4$ under hydrostatic pressure has revealed the existence of a special confluent point, denoted by L^* in the pressure-temperature (p-T) phase diagram, among the prototypical normal phase, the incommensurate phase, and the commensurate phase characterized by the wave vector $q=c^*/3$. With increasing pressure, the incommensurate phase with $q<c^*/3$ decreases its own stable temperature range and vanishes at L^*. The incommensurate region with $q>c^*/3$ appears at L^* and widens with increasing pressure. On the p-T phase diagram the second-order normal-incommensurate and the first-order incommensurate-commensurate phase lines meet at L^*. The wave vector in both incommensurate regions goes continuously to $c^*/3$ and the jump of the satellite intensity on the first-order incommensurate-to-commensurate phase transition becomes small, as the L^* point is approached. These experimental facts show that the L^* point is a multicritical point in incommensurate systems. These features of the obtained phase diagram are different from those of the universal one for $[N(CH_3)_4]_2MCl_4$ (M=Mn, Fe, and Zn) reported previously. [S0163-1829(96)06634-9]

I. INTRODUCTION

Tetramethylammonium tetrachlorocuprate $[N(CH_3)_4]_2CuCl_4$ $[(TMA)_2CuCl_4]$, which belongs to the A_2BX_4 type dielectrics, exhibits the structurally commensurate (C) incommensurate (IC) phase transition. The highest-temperature phase is the prototypical normal phase (N phase), which has the β-K_2SO_4 structure with space group $Pmcn$. With decreasing temperature, the successive phase transitions take place to the IC phase modulated along the c axis and characterized by the wave vector $q=(1-\delta)c^*/3$, to the ferroelastic C phase by $q=c^*/3$ (1/3C phase), and then to the unmodulated monoclinic phase at 27 °C, 20.5 °C, and −11 °C, respectively.[1–4] The pressure-temperature (p-T) phase diagram was reported by the optical and ultrasonic measurements.[5] With increasing pressure, the IC phase becomes narrow and finally vanishes at a triple point, where the N, IC, and 1/3C phases meet.

Such a confluent point is expected to be a multicritical point in incommensurate systems. The Lifshitz point[6] is a special multicritical point, which is well investigated theoretically, where N ($q=0$), C ($q=q_0$), and IC ($q\neq q_0$) phases meet and these phase lines join with a common tangent. As the Lifshitz point is approached, the incommensurate wave vector q continuously approaches to q_0. Other types of multicritical points in incommensurate systems were studied phenomenologically,[7,8] but no experimental evidence of such points has been reported.

It is known that $(TMA)_2MCl_4$ (M=Mn, Fe, Co, and Zn) compounds also have various C and IC phases depending on pressure and temperature. A prominent feature of the transition sequences of these compounds can be plotted on a universal p-T phase diagram.[9] In the previous paper,[10] we showed that the universal diagram contains many C phases with long periods and exhibits the devil's flower[11] behavior. However, the p-T phase diagram[5] of $(TMA)_2CuCl_4$ seems to be different from the universal one. The previous dielectric measurement[12] suggested that there is an additional pressure-induced phase transition in $(TMA)_2CuCl_4$. It is still unclear whether the phase diagram for M=Cu is included in the universal one.

In order to examine the existence of a multicritical point and to explore additional pressure-induced phases, we carried out x-ray-diffraction experiments of $(TMA)_2CuCl_4$ up to about 320 MPa by a careful measurement of satellite reflections as functions of pressure and temperature. We found an additional IC region that appears at its confluent point and widens with increasing pressure. As the confluent point is approached, the wave vector in both IC regions characterized by $q>c^*/3$ and $q<c^*/3$ continuously goes to $c^*/3$ and the jumps on the first-order IC-to-1/3C transition become small. These facts suggest that such a point is a special multicritical point in incommensurate systems. The differences between the obtained p-T phase diagram for M=Cu and the

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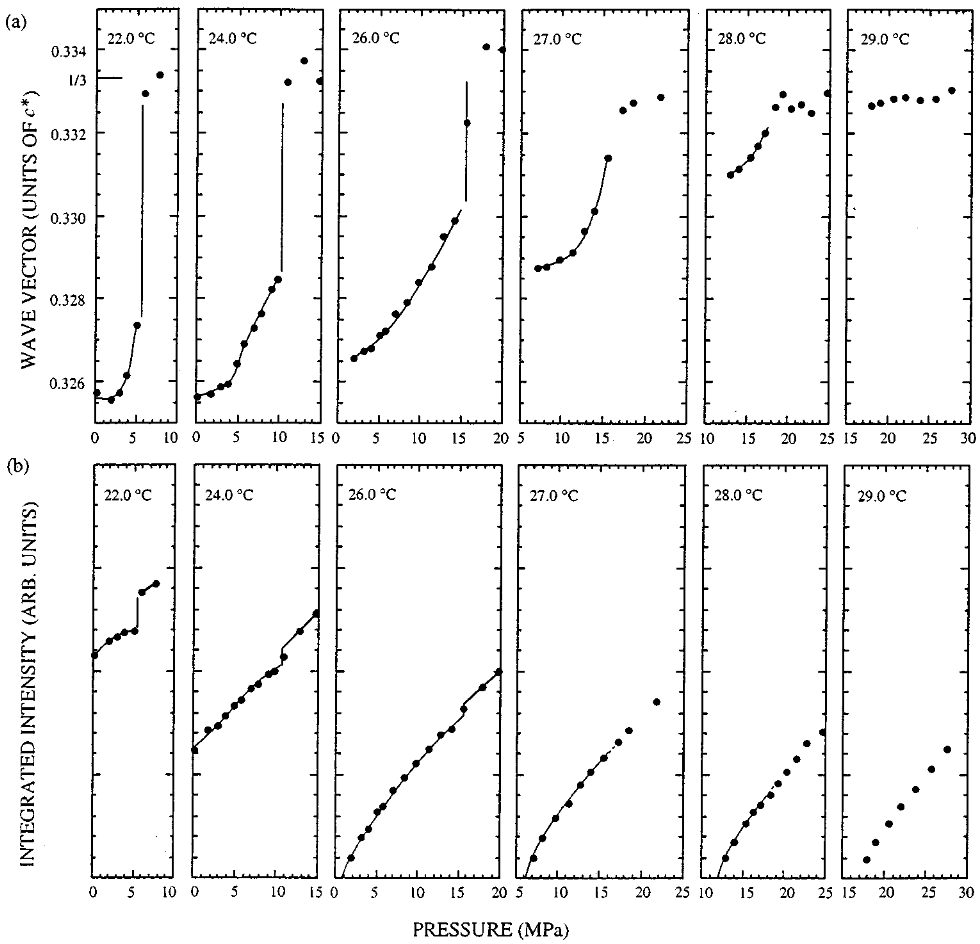

FIG. 1. Pressure dependence of (a) the wave vector and (b) the integrated intensity of the first-order satellite reflection at $(4,0,1-q/c^*)$ in the incommensurate region denoted by IC_{I} at 22.0, 24.0, 26.0, 27.0, 28.0, and 29.0 °C in $(TMA)_2CuCl_4$.

universal one[10] for M=Mn, Fe, and Zn are discussed.

II. EXPERIMENT

Single crystals of $(TMA)_2CuCl_4$ were grown by a slow evaporation from an aqueous solution of $N(CH_3)_4Cl$ and $CuCl_2$ at 30.0 °C. The sample trimmed about 0.3 mm^3 was mounted in a beryllium-cylinder high-pressure cell[13] so that the scattering plane was (101) plane. The sample was in contact with silicone oil filled in the pressure cell as pressure transmitting fluid. The pressure and temperature were measured with a Bourdon pressure gage and a copper-constantan thermocouple, respectively. The precision was as high as 0.2 MPa and 0.05 °C. X-ray-diffraction measurement was carried out on a double axis diffractometer with Mo $K\alpha$ radiation (40 kV, 30 mA) monochromatized by the 002 reflection of a pyrolytic graphite crystal. The experimental setup was nearly the same as the previous one described in Ref. 10.

The relatively intense first-order satellite at $(4,0,1-q/c^*)$ was measured along the modulation direction of c^*. The 400 and 402 Bragg reflections were also observed as reference points. Most of the measurements were carried out by varying pressure at several fixed temperatures. The sample was annealed for several hours in the N phase before each new measurement to reduce the memory effect[14] and the radiation damage effect.[15] These effects have been known to split the satellite reflection into several metastable components and to induce the stepwise behavior of the incommensurate wave vector as a function of temperature. In the present experiment, these effects were not seriously observed because the satellite obviously composed of a single peak smoothly varying as a function of pressure in the whole measurement.

III. RESULTS

First we measured the temperature variation of the satellite reflection from the sample in the pressure-cell at atmospheric pressure. The phase transition from the N to IC phase took place at about 26.0 °C. The satellite position was almost independent of temperature and jumped from $q/c^*=0.325$ to 1/3 at 19.5 °C. This result is in good agreement with that previously reported by neutron diffraction.[4] In this paper, this IC region to be stable at atmospheric pressure is denoted by IC_{I} in order to distinguish from another one found in this study, denoted by IC_{II}.

Figure 1 shows the pressure dependence of the wave vector and the integrated intensity of the satellite reflection in the IC_{I} region. The satellite appears at the N-to-IC_{I} transition pressures and its intensity increases continuously with increasing pressure. The gradual increase of the satellite in-

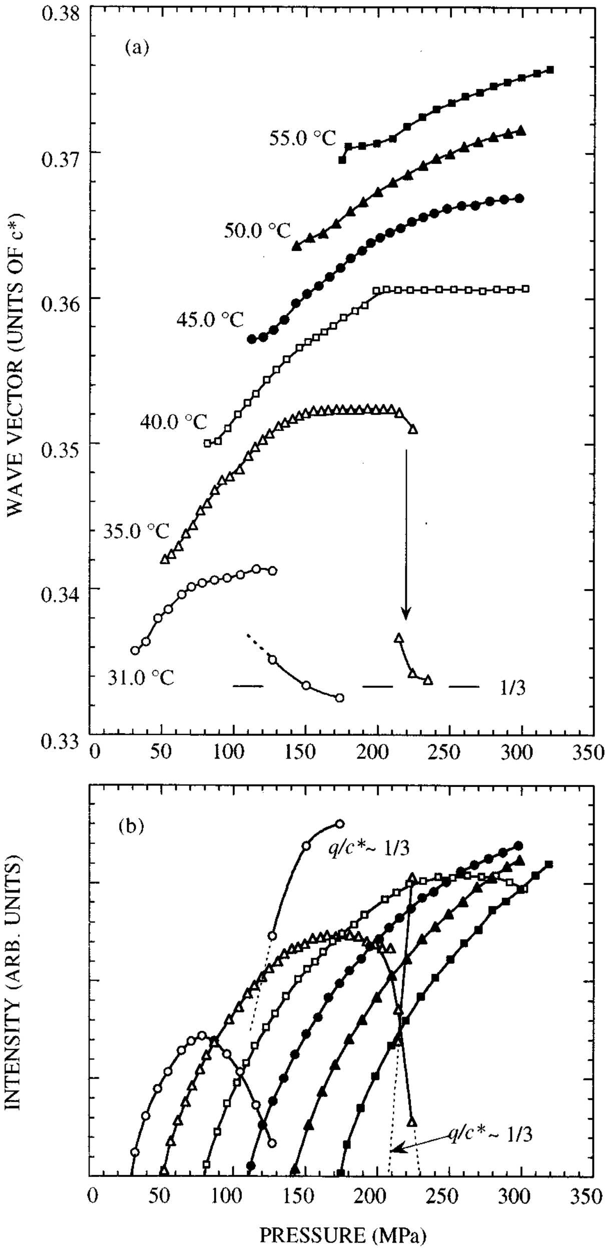

FIG. 2. Pressure dependence of (a) the wave vector and (b) the integrated intensity of the satellite reflection in the IC_{II} region in $(\mathrm{TMA})_2\mathrm{CuCl}_4$.

tensity and critical scattering were observed near the phase transition pressure, suggesting that the phase transition between the N and IC_{I} phases is of second order. As shown in Fig. 1(a), the wave vector increases monotonically with increasing pressure, and then jumps to $c^*/3$, associated with the IC_{I}-to-$1/3C$ phase transition. Discontinuous change of the satellite intensity shows that this phase transition is of first order. The discontinuity of the satellite intensity, however, becomes small for higher temperatures as shown in Fig. 1(b). The wave vector also exhibits similar behavior. These facts imply that the first-order nature of the IC_{I}-to-$1/3C$ transition becomes a second-order one as the temperature increased. The higher-order satellites up to fifth order were observed just below the IC_{I}-to-$1/3C$ phase transition pressures, where the incommensurate modulation is nonsinusoidal.

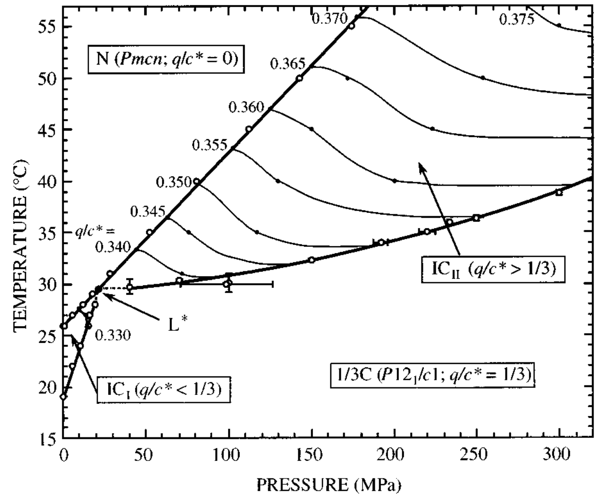

FIG. 3. Pressure-temperature phase diagram of $(\mathrm{TMA})_2\mathrm{CuCl}_4$. Bold and thin lines represent the phase boundaries and contours of equal incommensurate wave vector, respectively. The N phase, the $1/3C$ phase, and the IC phase with two regions, IC_{I} and IC_{II}, meet at the L^* point.

The stable pressure range of IC_{I} decreases with increasing temperature and finally vanishes. Applying further pressure, we found the reappearance of the IC region, denoted by IC_{II}. The pressure dependence of the wave vector and the satellite intensity was measured in a similar way up to about 320 MPa and 55.0 °C as shown in Fig. 2. The IC_{II} region is characterized by the wave vector $q > c^*/3$ in contrast to the IC_{I} region by $q < c^*/3$. The incommensurate wave vector continuously increases with increasing pressure and becomes independent of pressure apart from the N-IC_{II} phase transition pressures. Critical scattering and no apparent anomaly of the integrated intensities show the N-to-IC_{II} phase transition is of second order. The transition to the $1/3C$ phase was observed at 31.0 and 35.0 °C. The coexistence of the peaks attributed to the IC_{II} and $1/3C$ phases suggests that its phase transition is of first order. The higher-order satellites were also observed near the IC_{II}-$1/3C$ phase transition pressures.

The obtained p-T phase diagram of $(\mathrm{TMA})_2\mathrm{CuCl}_4$ is shown in Fig. 3. Bold lines indicate the phase boundaries to separate the N phase, the IC phase with two regions denoted by IC_{I} and IC_{II}, and the $1/3C$ phase. Error bars mean the range of the coexistence of the IC_{II} and $1/3C$ phases. The N-IC_{I} and N-IC_{II} phase lines are linear with a same slope of 0.168(1) °C/MPa, and the IC_{I}-$1/3C$ with 0.462(18) °C/MPa. The most interesting feature of the phase diagram is that the second-order N-IC and first-order IC-$1/3C$ phase transition lines converge at a point denoted by $L^*(p^*,T^*) = (23.4$ MPa, 30.0 °C$)$ within the experimental accuracy.

The thin lines in the IC_{I} and IC_{II} regions shown in Fig. 3 represent contour lines of the equal wave vector from $q/c^* = 0.330$ to 0.375 at intervals of 0.005. The wave vector in both IC regions deviates from $c^*/3$ apart from the L^* point. In order to precisely examine the variation of the wave vector on approaching the L^* point, the deviation from $c^*/3$ along the phase lines is plotted in Fig. 4 as a function of a

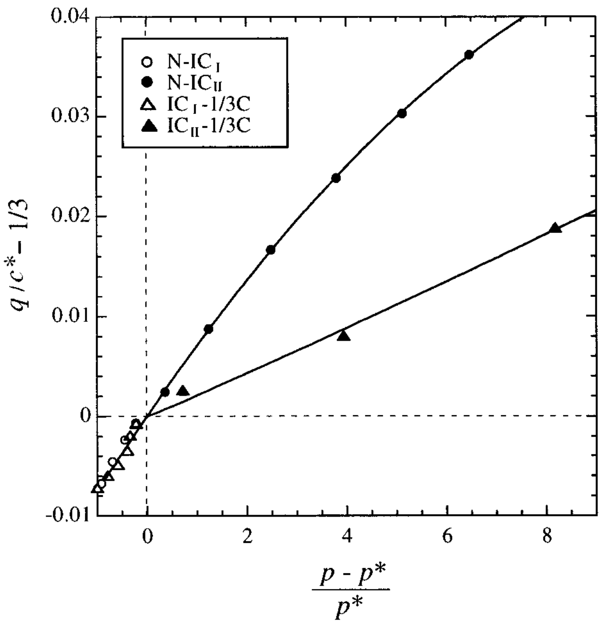

FIG. 4. The deviation of the incommensurate wave vector from $c^*/3$ along the phase boundaries as a function of a reduced pressure $(p\text{-}p^*)/p^*$, where p^* is the pressure of the L^* point. All lines converge on the origin, showing that the wave vector in both IC_{I} and IC_{II} regions continuously goes to $c^*/3$ as the L^* point is approached.

reduced pressure of $(p\text{-}p^*)/p^*$. The wave vectors on the $N\text{-}IC_{\mathrm{I}}$ and $N\text{-}IC_{\mathrm{II}}$ phase lines increase with increasing pressure and follow a same monotonical function. All the lines converge at the origin of the figure. This fact implies that the wave vector in both IC regions continuously goes to $c^*/3$ as the L^* point is approached.

When the transition to the $1/3C$ phase occurs, the Bragg and superlattice reflections split owing to the creation of the ferroelastic domains. The splitting angle gives the deviation of the monoclinic angle from 90°, $\Delta\beta$, which corresponds to the spontaneous shear strain in the ferroelastic $1/3C$ phase. The absolute value of $\Delta\beta$ along the IC_{I}- $1/3C$ and IC_{II}-$1/3C$ phase lines is plotted in Fig. 5 as a function of pressure. The deviation $\Delta\beta$ also approaches to zero continuously as the L^* point is approached within the $1/3C$ phase.

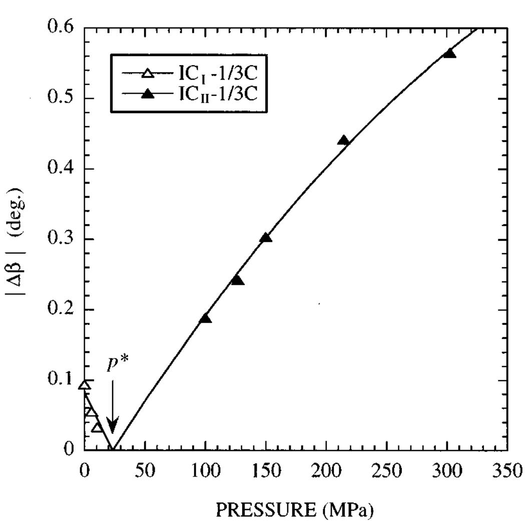

FIG. 5. The absolute value of the deviation angle of the monoclinic angle from 90°, $|\Delta\beta|$, in the ferroelastic $1/3C$ phase along the IC_{I}-$1/3C$ and IC_{II}-$1/3C$ phase lines. At the L^* point, $|\Delta\beta|$ appears to be zero.

IV. DISCUSSION

The p-T phase diagram of $(TMA)_2CuCl_4$ has a characteristic point denoted by L^*, whose features are as follows. (1) The IC phase vanishes and reappears at L^* with increasing pressure. (2) The second-order $N\text{-}IC$ phase line and the first-order IC-$1/3C$ phase line meet at L^*. (3) The jumps on the first-order IC-to-$1/3C$ transition become small as the L^* point is approached. (4) The wave vector in both IC regions continuously goes to $c^*/3$ as the L^* point is approached.

These experimental facts for the L^* point can be understood by a phenomenological Landau theory. Toledano[8] discussed various multicritical points in incommensurate systems by expressions for the coefficient of the quadratic order parameter $\alpha(q)$, which depends on the wave vector q. The function $\alpha(q)$ is expanded as a function of q:

$$\alpha(q)=\alpha_0(T,P)+\Sigma\,\alpha_n(T,P)(q-q_0)^n, \tag{1}$$

where q_0 is a commensurate wave vector and P is an external parameter, e.g., hydrostatic pressure. Taking into account terms of degree n means that the free-energy density includes invariants of the quadratic order parameter and of the nth order derivative with respect to space coordinate. When odd terms in powers of $q-q_0$ are allowed in (1), the simplest case is

$$\alpha(q)=\alpha_0(T,P)+\alpha_1(q-q_0)+\alpha_2(q-q_0)^2, \tag{2}$$

where $\alpha_2>0$ for stability of the IC phase. The linear term in (2) corresponds to the Lifshitz invariant term in the Landau free energy. The temperature dependence of α_0 is assumed as

$$\alpha_0=\alpha_0'(T-T_0). \tag{3}$$

The second order $N\text{-}IC$ transition takes place at T_i given by

$$T_i=T_0+\alpha_1^2/(4\alpha_0'\alpha_2) \tag{4}$$

and the wave vector q_i is

$$q_i=q_0-\alpha_1/(2\alpha_2). \tag{5}$$

The realization of the L^* point is considered to be essentially related to the pressure dependence of the coefficient α_1 of the Lifshitz term. The coefficient α_1 is assumed to be positive and to decrease monotonically with increasing pressure, and α_0' and α_2 not to be sensitive to the pressure. As α_1 decreases, the wave vector q_i increases to q_0 and the width of the IC phase decreases. When α_1 is zero, i.e., the Lifshitz term vanishes, the wave vector q_i is $q_0(=c^*/3)$ and the direct $N\text{-}C$ transition takes place. With increasing pressure, the coefficient α_1 changes its sign and decreases. The IC phase reappears and increases the own stable range and the wave vector q_i increases from q_0. Consequently the L^* point is considered to be a multicritical point, where both α and α_1 vanish.

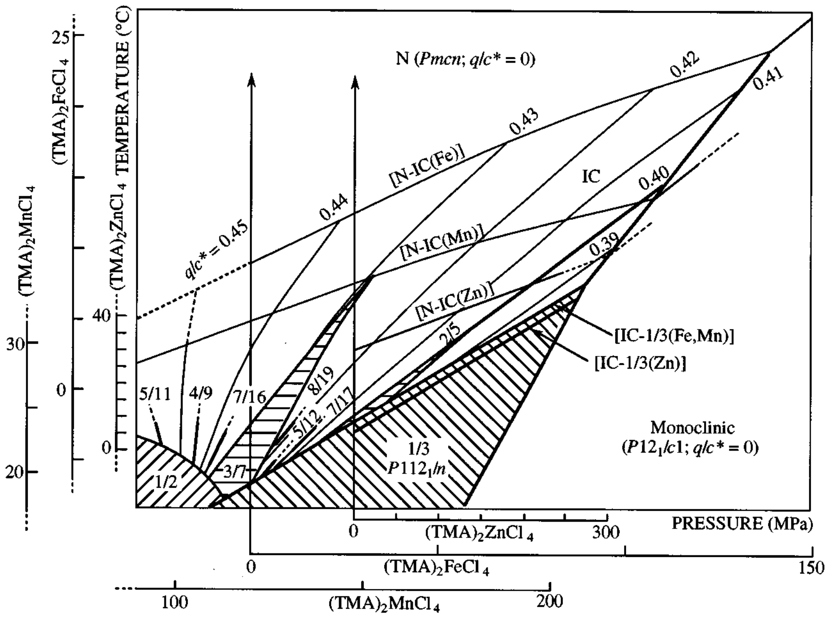

FIG. 6. The universal p-T phase diagram for $(TMA)_2MCl_4$ (M=Mn, Fe, and Zn) reported previously (Ref. 10). Hatched areas and bold lines marked by the fractions are the C phases. The thin lines in the IC area denote contours of equal wave vector. The pressure and temperature scales are shown in the bottom and the left for each compound. The lines marked by $[N\text{-}IC(M)]$ and $[IC\text{-}1/3(M)]$, M=Mn, Fe, and Zn, represent the N-IC and IC-1/3C phase boundaries for each compound. This universal phase diagram for M=Mn, Fe, Zn is different from that for M=Cu shown in Fig. 3.

The reappearance of the IC phase shows that the L^* point is different from the Lifshitz point defined by Hornreich *et al.*[6] The Lifshitz point is defined by the condition $\alpha(T,P)=\alpha_2(T,P)=0$ for the expression $\alpha(q)=\alpha_0(T,P)+\alpha_2(q-q_0)^2+\alpha_4(q-q_0)^4$, which includes no odd terms, i.e., the Lifshitz condition is satisfied.[8]

The second-order N-IC phase line is considered to be tangent to the first-order IC-1/3C phase line at the L^* point, but it cannot be concluded experimentally. It is difficult to detect the phase transition between the IC and 1/3C phases near the L^* point. The first-order jumps on the IC-to-1/3C phase transition become small as the L^* point is approached. This fact suggests that the direct N-to-1/3C transition is second.

An interesting feature of the $(TMA)_2MCl_4$ (M=Mn, Fe, Co, and Zn) family is that the interrelation of the p-T phase diagrams of different metals M can be plotted on a universal phase diagram.[9,10] Figure 6 shows the universal diagram for M=Mn, Fe, and Zn reported previously.[10] The hatched areas and the bold lines marked by fractions are C phases. The thin lines in the IC area denote contours of equal modulation wave vector. The phase transition of the Co compound under pressure is considered to be also well represented by this universal diagram.[9,10]

Although $(TMA)_2CuCl_4$ belongs to the above family according to the chemical composition, the p-T phase diagram of this compound is dissimilar to the universal one, which does not have two IC regions and the L^* point. The incommensurate wave vector, for M=Cu, increases from about $0.325c^*$ to $0.375c^*$ with increasing pressure in the observed region. On the other hand, the wave vector on the universal phase diagram decreases from about $0.46c^*$ to $0.375c^*$ with pressure. The space group of the 1/3C phase[3] for M=Cu is different from that for the universal diagram. An explanation of the unusual behavior of $(TMA)_2CuCl_4$ has not been established from a crystallographic point of view. One of the reasons is considered to be attributed to the strong distortion of the $CuCl_4^{2-}$ tetrahedron.[16]

The universal phase diagram has many C phases with long periods and exhibits the devil's flower[11] behavior. For M=Cu, only one C phase, characterized by $q=c^*/3$, is observed. At higher pressure, $(TMA)_2CuCl_4$ is expected to have additional C phases with long periods in the IC_{II} region.[17] The existence of such C phases is predicted by the theoretical models to provide the transition sequences of the A_2BX_4 type dielectrics.[18]

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