

## Characterization of the incommensurate phase of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$

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$[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$  is incommensurately modulated between  $T_c = 73(1)^\circ\text{C}$  and  $T_i = 108(1)^\circ\text{C}$ . Isomorphous with  $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ ,  $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$  transforms from a commensurately modulated  $P2_1/c$  phase to the incommensurate phase at  $T_c$  and to an unmodulated  $Pm\bar{c}n$  phase at  $T_i$ . The modulation vector  $\mathbf{q}$  decreases discontinuously from the lock-in value of  $\mathbf{c}^*/3$  at  $T_c$  to the incommensurate value of  $0.258(2)\mathbf{c}^*$ , then decreases continuously to  $0.179(3)\mathbf{c}^*$  at  $T_i$ , resulting in a very-long-wavelength modulation of the sublattice. The range of continuous variation of the incommensurate modulation vector  $0.079\mathbf{c}^*$  is apparently the largest of any  $A_2BX_4$  compound reported to date.

Many compounds in the  $A_2BX_4$  family (where  $A$  is a monovalent cation and  $BX_4$  a dinegative tetrahedral anion) exhibit incommensurate phases,<sup>1,2</sup> the most studied example being  $\text{K}_2\text{SeO}_4$ .<sup>2,3</sup> These compounds exist in a pseudohexagonal phase (orthorhombic,  $Pm\bar{c}n$ ,  $b \approx \sqrt{3}a$ ) at high temperature, but undergo a transition to an incommensurately modulated phase at lower temperature. A characteristic of the incommensurate phase is the appearance of satellite (secondary) Bragg reflections with irrational Miller indices ( $hkl$ ) relative to the primary reflections of the unmodulated phase. For example, for (one-dimensional) incommensurate modulation along the  $c$  axis in an orthorhombic crystal, satellite reflections will have indices  $(hkl \pm m\delta)$ , where  $\delta = |\mathbf{q}|/|\mathbf{c}^*|$ ,  $h$ ,  $k$ ,  $l$ , and  $m$  integers. The Miller indices of the satellite reflections vary with temperature in the incommensurate phase, but lock into a constant value on entering a commensurate phase at lower temperature. In this paper the reverse of this sequence is considered;  $T_c$  corresponds to the commensurate-incommensurate transition temperature on heating and  $T_i$  to the incommensurate-unmodulated pseudohexagonal transition.

An extensively studied subgroup of the  $A_2BX_4$  family is  $(\text{TMA})_2MX_4$  (TMA is tetramethylammonium,  $M$  a first-row transition metal, and  $X$  a halide).<sup>1</sup> The  $(\text{TMA})_2M\text{Cl}_4$  compounds, excluding  $M = \text{Cu}$ , may be placed on a common schematic pressure-temperature phase diagram.<sup>3</sup> The phase sequences of the corresponding deuterated compounds are found to occur at a markedly lower effective pressure on the phase diagram relative to their undeuterated analogues.<sup>4</sup> This pronounced isotope effect initially was thought to be due to an increase in lattice volume upon deuteration. However, the corresponding bromide compounds exhibit very different  $P$ - $T$  phase behavior indicating a more complex dependence on cation and anion size.<sup>5</sup> This observed variation of phase behavior with change in cation or anion size prompted us to synthesize a series of analogous compounds using the larger tetramethylphosphonium (TMP) cation. This Communication reports preliminary studies

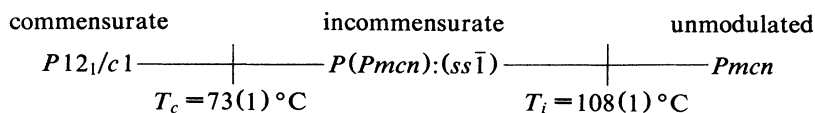
on the first compound in this series,  $(\text{TMP})_2\text{CuCl}_4$ .

Stoichiometric amounts of tetramethylphosphonium chloride (Aldrich) and anhydrous copper(II) chloride were mixed in 1-propanol. The resulting yellow precipitate was filtered, washed with 1-propanol, dried *in vacuo*, and recrystallized from water. Differential scanning calorimetry (DSC) measurements were obtained on a Perkin-Elmer DSC 7 and a Perkin-Elmer DSC 1 interfaced to an IBM personal computer<sup>6</sup> using a scan rate of  $5^\circ\text{C}/\text{min}$ . Both instruments were calibrated using the melting point of pure indium metal as a reference. Single-crystal x-ray studies were carried out on a Nicolet R3 four-circle diffractometer. The crystal was maintained at a desired temperature with a device, attached to the  $\chi$  circle of the diffractometer, which directed a stream of heated, dry air along the  $\phi$  axis of the diffractometer and onto the crystal.

Lattice parameters and the incommensurate modulation vector,  $\mathbf{q}$ , were analyzed in the following manner. 13–14 sublattice (primary) reflections with  $53^\circ < 2\theta < 83^\circ$ , Cu  $K\alpha$  radiation, were used for centering and lattice-parameter determination by least-squares analysis. A further 8–11 satellite reflections with  $20^\circ < 2\theta < 51^\circ$  were then indexed with respect to the sublattice. The mean deviation of the  $l$  indices from integer values for satellite reflections is graphed versus temperature in Fig. 1. The first-order satellite reflections used correspond to  $(hkl \pm \delta)$ ,  $\delta = |\mathbf{q}|/|\mathbf{c}^*|$ , where  $\mathbf{c}^*$  corresponds throughout this paper to the sublattice. The standard deviation of the mean for  $\mathbf{q}$  varied from  $0.002\mathbf{c}^*$  to  $0.004\mathbf{c}^*$ . The heating-cooling-reheating cycle required  $\approx 9$  days per crystal.

DSC results are shown in Fig. 2 where two transitions, similar to those in other  $A_2BX_4$  compounds<sup>7</sup> are clearly seen. From repetitions of the experiment the following results and their uncertainties were obtained. For the assumed first-order transition from commensurate to incommensurate phases at  $T_c = 72(1)^\circ\text{C}$  (onset temperature),  $\Delta S_c = 1.2(2) \text{ JK}^{-1}\text{mol}^{-1}$ . For the suspected continuous transition at  $T_i = 108(1)^\circ\text{C}$  (peak temperature), the en-

entropy of transition is theoretically zero, but calculating indirectly from peak area,  $\Delta S_i = 4(2) \text{ JK}^{-1} \text{ mol}^{-1}$ . Because of the experimental uncertainty of these results, more qualitative remarks may be made concerning the shape of the DSC curve than may be made concerning actual calculated enthalpies and entropies of transition. The incommensurate-unmodulated transition shows the  $\lambda$  shape with a long low-temperature tail typical of continuous transitions. The sharper commensurate-incommensurate transition is typical of a first-order transition but includes a small high-temperature tail consistent with the discommensurations<sup>8,9</sup> (phase solitons) expected in



In each phase the following cell constants were obtained: 110(1)°C, unmodulated, orthorhombic phase;  $a = 9.296(2) \text{ \AA}$ ,  $b = 15.670(4) \text{ \AA}$ , and  $c = 12.782(2) \text{ \AA}$ ; 73(1)°C, incommensurate, orthorhombic phase,  $a = 9.280(6) \text{ \AA}$ ,  $b = 15.616(8) \text{ \AA}$ , and  $c = 12.598(6) \text{ \AA}$ ; 21(2)°C, commensurate, monoclinic phase,  $a = 9.251(3) \text{ \AA}$ ,  $b = 15.569(5) \text{ \AA}$ ,  $c = 37.582(13) \text{ \AA}$ , [ $3 \times 12.527(4) \text{ \AA}$ ], and  $\beta = 90.23(3)^\circ$ . Axial lengths decrease continuously with temperature from above  $T_i$  to  $T_c$ . At  $T_c$  there is a discontinuous change in  $\beta$  and a kink in the length of the  $c$  axis. From reflection extinction conditions and structure determinations the space groups of the commensurate and unmodulated phases are  $P2_1/c$  and  $Pm\bar{c}n$ , respectively. The incommensurate phase is not assignable to a normal three-dimensional space group; nevertheless for an incommensurately modulated crystal a "superspace group"<sup>10</sup> may be assigned to account for the symmetry of the crystal. From a preliminary analysis of extinction conditions of primary and satellite reflections, the superspace group at 100(1)°C is  $P(Pm\bar{c}n):(s\bar{s}\bar{1})$ , isomorphic with the incommensurate phase of several  $A_2BX_4$  compounds including  $\text{Rb}_2\text{ZnBr}_4$  (Ref. 11) (upon the

the incommensurate regime. Qualitatively, these results compare well with adiabatic calorimetry results for  $\text{Rb}_2\text{ZnBr}_4$ ,  $\text{Rb}_2\text{ZnCl}_4$ , and  $\text{K}_2\text{SeO}_4$ .<sup>7</sup> Quantitatively, however, the ratio of  $\Delta S_i/\Delta S_c = 3(2)$  for  $(\text{TMP})_2\text{CuCl}_4$  is much less than the precise results obtained for these compounds:  $\Delta S_i/\Delta S_c = 73$  and 21 for  $\text{K}_2\text{SeO}_4$  and  $\text{Rb}_2\text{ZnCl}_4$ , respectively.

Our x-ray studies confirm that  $(\text{TMP})_2\text{CuCl}_4$  undergoes transitions connecting phases having characteristic space groups isomorphic to  $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$ . The following series has been identified:

transformation  $\mathbf{a} \leftrightarrow \mathbf{b}$ ) and  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  (Ref. 12) (upon the transformation  $\mathbf{q} = \mathbf{q} - \mathbf{c}^*$ )<sup>13</sup> and agreeing with Landau theory.<sup>14</sup>

The measured values of  $\mathbf{q}$  at different temperatures for two different crystals are shown in Fig. 1. On heating  $T_i$ ,  $T_c$ , and  $\mathbf{q}$  at  $T < T_c$  and  $T = T_i$  are equivalent within experimental error for the two samples. Cooling behavior is more divergent. Because the crystal represented by open symbols was grown more rapidly and exhibits a larger hysteresis (see below), it is believed to contain more impurities and/or defects than the crystal represented by closed symbols. The modulation wave vector for the "impure" crystal remained incommensurate even after cooling to 25(1)°C, 48°C below  $T_c$ .  $\mathbf{q}$  remained constant for both crystals on reheating back to  $T_c$ ;  $\mathbf{q}$  then began to retrace the original heating curve. Reheating data points are not included in Fig. 1.

The experimental discrepancy between the two crystals may be explained with a discommensuration (phase soliton) picture.<sup>8,9</sup> Impurities and/or defects in the crystal pin discommensurations, and this pinning effect is greatest at temperatures close to  $T_c$ . Thus, as the temperature is

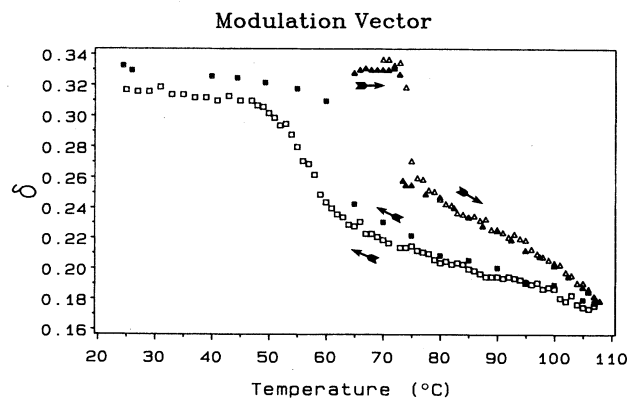


FIG. 1. Temperature dependence of the modulated wave vector,  $\mathbf{q}$ , of  $(\text{TMP})_2\text{CuCl}_4$ .  $\delta = |\mathbf{q}|/|\mathbf{c}^*|$ . Different symbols represent different crystals. Triangular symbols represent initial heating. Square symbols represent cooling.

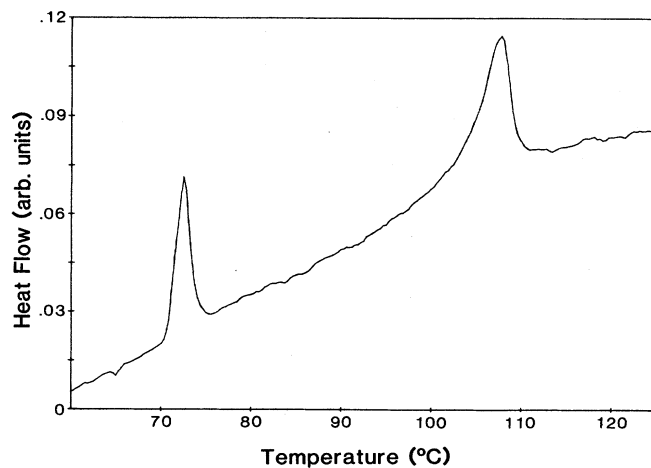


FIG. 2. DSC results for  $(\text{TMP})_2\text{CuCl}_4$  spanning  $T_c$  and  $T_i$ .

TABLE I. Transition temperatures and modulation wave vectors for selected  $A_2CuX_4$  compounds.

Compound	Symmetry $T < T_m$	$T_m$ (°C)	Symmetry $T < T_c$	$T_c$ (°C)	$q_c^a$	$\Delta q^b$	$T_i$ (°C)	$q_i^c$	References
$[N(CH_3)_4]_2CuBr_4$	$P2_1/c$	-36 <sup>d</sup>	$Pbc2_1$	-28	$b^*/2$	$0.07b^{*d}$	-1.0	$0.38b^*$	15,16
$[N(CD_3)_4]_2CuBr_4$		-36 <sup>d</sup>		-26	$b^*/2$	$0.06b^*$	-0.8	$0.38b^*$	17
$[N(CH_3)_4]_2CuCl_4$			$P2_1/c$	18.1	$c^*/3$	$0.007c^*$	25.9	$0.326c^*$	4,18,19
$[N(CD_3)_4]_2CuCl_4$				20.0			26.1		4
$[P(CH_3)_4]_2CuCl_4$			$P2_1/c$	73(1)	$c^*/3$	$0.075c^*$	108(1)	$0.179c^*$	this work

<sup>a</sup> Wave vector at  $T_c$ .

<sup>b</sup> Discontinuous decrease in wave vector on heating.

<sup>c</sup> Wave vector at  $T_i$ .

<sup>d</sup> On cooling.

increased above  $T_c$ , impurities preclude the equilibrium formation of discommensurations, so the modulation vector changes continuously over a finite temperature range rather than discontinuously at  $T_c$ . Since the pinning effect of impurities on discommensurations decreases as  $T_i$  is approached, the behavior of the modulation vector merges for both samples. The large difference between samples on cooling is again explained by impurities and/or defects restraining the diffusion and annihilation of discommensurations. Further comments will concern the more carefully grown crystal (closed symbols).

The incommensurate behavior of  $(TMP)_2CuCl_4$  shows both significant similarities as well striking contrasts in comparison with other  $A_2BX_4$  compounds. As temperature is increased above  $T_c$ ,  $q$  decreases abruptly from  $q = c^*/3$ , in an analogous fashion to  $[N(CH_3)_4]_2CuCl_4$ . The discontinuous decrease is much greater for  $(TMP)_2CuCl_4$  however:  $0.075c^*$  (to  $q = 0.258(2)c^*$ ) vs  $0.007c^*$  (to  $q = 0.326c^*$ ). In the incommensurate phase  $q$  for the TMP salt monotonically decreases to a value of  $0.179(3)c^*$  at  $T_i$ . In contrast,  $q$  is almost temperature independent for the TMA salt. The range of  $q$  in the incommensurate phase  $0.079c^*$  is larger, and the value of  $q$  at  $T_i$  is smaller, than for any other  $A_2BX_4$  compound studied to date. Transition temperatures and modulation wave vectors for known incommensurate  $A_2CuX_4$  systems are summarized in Table I. For these compounds it can be

seen that the transition temperatures,  $T_i$  and  $T_c$  (or  $T_m$ ), increase as the ratio of cation-to-anion size increases. No such obvious correlation is apparent with respect to modulation direction.

Figure 3 represents the intensity of three first-order satellite reflections as a function of temperature. The solid lines correspond to best fits of the critical function  $I = c(T_i - T)^{2\beta}$ ,  $T < T_i$ , with  $c$ ,  $2\beta$ , and  $T_i$  as parameters. Results are tabulated in Table II.  $2\beta$  is predicted on theoretical grounds, based on a three-dimensional ferromagnetic  $XY$  model, to be 0.70.<sup>20</sup> The deviation from theory for the values of  $2\beta$  reported here is greater than in other  $A_2BX_4$  compounds. For example,  $2\beta = 0.67(2)$  in  $(TMA)_2CuBr_4$  (Ref. 6) and  $0.55(3)$  in its deuterated analogue.<sup>8</sup> The dependence of  $2\beta$  on individual (first-order) reflections has not been previously reported and represents a further contradiction with theory. A possible problem in the experiment concerns the  $\omega$  scanning technique used to measure intensities. Temperature-dependent peak broadening along  $c^*$  is expected in the incommensurate region and care should have been taken to correspondingly scan along  $c^*$  to avoid possible broadening dependence in intensity measurements. Nevertheless, an analysis of  $(TMA)_2ZnCl_4$  employing a  $\theta$ - $2\theta$  scan yielded results ( $2\beta = 0.70$  and  $0.73$ ) in good agreement with theory.<sup>12</sup> Other causes of discrepancy could include extinction effects, multiple scattering, and critical inelastic (diffuse) scattering. Scans along  $c^*$  of several satellite reflections of varying intensity along with their Friedel equivalents should allow better determinations of  $T_i$  and  $2\beta$ .

Crystal structure determinations for the three phases of  $(TMP)_2CuCl_4$  discussed in this paper will be the subject of future work as well as a continued study of physical properties including adiabatic calorimetry with an em-

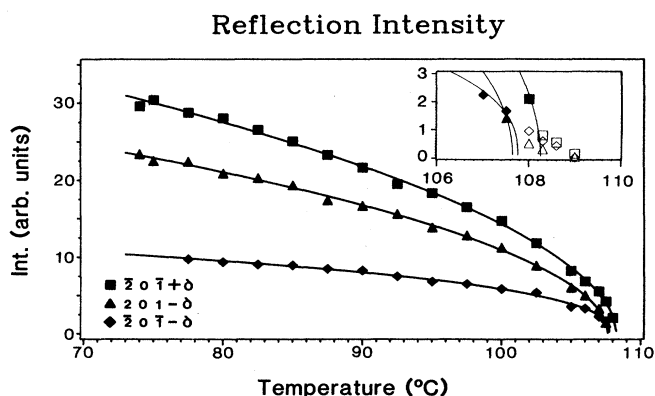


FIG. 3. Temperature dependence of the integrated intensities of three satellite reflections of  $(TMP)_2CuCl_4$  (on heating).  $\delta = |q|/|c^*|$ . Solid lines fit to model explained in text. Open symbols not included in model fit.

TABLE II. Critical intensity behavior of selected first-order satellite reflections.

Reflection ( $hkl$ )	$2\beta$	$T_i$ (°C)
$201 - \delta^a$	0.51(1)	107.65(6)
$\bar{2}0\bar{1} + \delta$	0.53(1)	108.26(9)
$\bar{2}0\bar{1} - \delta$	0.39(2)	107.76(10)

<sup>a</sup>  $\delta = |q|/|c^*|$ .

phasis on the phenomenological Landau theory of phase transitions for theoretical explanation.

*Note added in proof.* Radiation damage may cause additional defects partly responsible for the thermal hysteresis of Fig. 1 and the peak broadening possibly responsible for the anomalous intensities (critical exponents) of Fig. 3 and Table II.<sup>21</sup>

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