

Thermal and diffraction studies of phase transitions in the incommensurate compound [P(CH₃)₄]₂CuCl₄

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(Received 2 July 1993; revised manuscript received 22 September 1993)

Calorimetric and x-ray-diffraction studies of the commensurate (C)-incommensurate (IC) and incommensurate (IC)-normal (N) phase transitions in [P(CH₃)₄]₂CuCl₄ are reported. The C-IC transition at $T = 346.20 \pm 0.25$ K is shown to be first order with a value of $\Delta_{tr}S = 3.70 \pm 0.09$ J K⁻¹ mol⁻¹. The IC-N transition at $T = 381.23 \pm 0.25$ K appears to be second order with $\Delta_{tr}S = 5.40 \pm 0.10$ J K⁻¹ mol⁻¹. The orders of the transitions are based on the calorimetric data and the lattice parameters; the latter show a discontinuity at the C-IC transition but only show a discontinuity in slope at the IC-N transition. An additional anomaly, of unknown origin, is observed in the heat-capacity data following particular thermal histories, but it is not observed by diffraction studies. Critical-point analysis of the intensity of the satellite diffraction peaks within about 6 K of the IC-N transition leads to the estimate that $2\beta = 0.54$. Similar analysis of the thermal data within 1 K of the transition shows that α' depends on the temperature range of the fit and $\alpha' < 0.04$. The temperature dependence of the effective values of the critical exponents, especially α' , and the discrepancies between observed α' and β values with predictions for a three-dimensional XY model show that data closer to T_c are required to carry out more complete critical-behavior analysis in this system.

I. INTRODUCTION

Compounds of the general formula A_2BX_4 (where A is a univalent cation and BX_4 is a divalent tetrahedral cation) can exhibit incommensurate (IC) structures. Indeed, this general family of compounds is the most thoroughly investigated group with IC structures.¹ The high-temperature normal (N) structure is pseudo-hexagonal (orthorhombic, $Pm\bar{c}n$, $b \approx \sqrt{3}a$); as the temperature is reduced, an IC phase is stabilized. At lower temperatures, the wave vector k_c of an unstable mode freezes in to give a commensurate (C) phase. For example, in K₂SeO₄ the C phase is induced by the instability of a mode with $k_c = a^*/3$, and the C phase is an improper ferroelectric.² In that case the C phase is characterized by its polarization. If the C phase is characterized by strain, then the C phase is an improper ferroelastic; [N(CH₃)₄]₂CuCl₄ is an example.^{3,4}

One extensively investigated subgroup of the A_2BX_4 family is [N(CH₃)₄]₂MX₄, where [N(CH₃)₄]⁺ is the tetramethylammonium ion, M is a first-row transition metal ion, and X is a halide. Excluding $M = \text{Cu}^{2+}$, the [N(CH₃)₄]₂MCl₄ compounds can be placed on a common pressure-temperature phase diagram,¹ indicating the possibility of a corresponding states treatment of the transitions in these materials. However, the phase transitions in the corresponding bromides show a more complex dependence on cation and anion sizes.⁵ In order to investigate in some detail the effect of cation and anion size, we have synthesized a series of analogous compounds with the larger tetramethylphosphonium cation [P(CH₃)₄]⁺. From previously reported⁶ preliminary results of the investigations of [P(CH₃)₄]₂CuCl₄ by dif-

ferential scanning calorimetry and observation of the temperature dependence of lattice parameters, this salt is known to present an incommensurate phase, intermediate in temperature between a commensurate and a normal phase. The known phase transitions in [Z(CH₃)₄]₂MX₄ have been summarized recently;⁷ curiously, [P(CH₃)₄]₂CuBr₄ apparently does not have an incommensurate phase.⁸ In this report we present the heat capacity of [P(CH₃)₄]₂CuCl₄ measured from 30 to 395 K, and more detailed results for the temperature dependence of the lattice parameters as determined by x-ray diffraction. A detailed analysis of the crystal structures for the C, IC, and N phases is presented elsewhere.⁹

II. EXPERIMENT

Synthesis

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, vacuum dried, and recrystallized from water. The sample's identity as [P(CH₃)₄]₂CuCl₄ was confirmed by single-crystal x-ray diffraction.¹⁰

X-ray diffraction

The x-ray-diffraction data were collected from a single crystal with a Nicolet R3m diffractometer with graphite monochromated CuK α radiation. Temperatures were maintained with a directed stream of heated dry air along the φ axis of the diffractometer onto the crystal. Temperatures were calibrated with a chromel-alumel thermocou-

ple, and temperature stability was ± 0.7 K over several days, with an accuracy of ± 1 K. Lattice parameters were determined between 293 and 433 K by least-squares refinement of up to 25 well-centered high-angle reflections. Standard and adapted Nicolet-Siemens programs^{10,11} were used for data collection.

Calorimetry

The heat capacity of 4.2753 g of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ was measured throughout the temperature range from 30 to 400 K in an adiabatic calorimeter that was operated in the heat pulse mode. The calorimeter has been described in detail elsewhere.¹² The accuracy of this calorimeter was tested previously by measuring the heat capacity of a sample of calorimetry conference (NBS-49) benzoic acid from 35 to 350 K; those measurements agreed with the literature to within 0.5%.¹² Most of the measurements were taken in the fully automated mode using temperature increments of around 1 to 6 K.

The same calorimeter also was operated in a continuous heating mode. In this mode the sample was heated continuously at about 2.5 K hr^{-1} and the heat capacity as a function of temperature, $C_p(T)$, was derived from the known heater power \dot{q} from the equation

$$\dot{q} = C_p(T) \frac{dT}{dt} \quad (1)$$

where the rate of change of temperature with respect to time, dT/dt , was approximated by $\Delta T/\Delta t$ calculated for small temperature increases ($\Delta T \text{ ca. } 0.2 \text{ K}$). Although this method is less accurate than adiabatic calorimetry and it has the further drawback that it gives peak temperatures of phase transitions that depend on the heating rate, the continuous heating method is very precise and can be used effectively to obtain high-resolution heat-capacity data. Therefore it was employed in this work to investi-

gate the critical behavior of the heat capacity around the incommensurate-normal (IC-N) phase transition.

III. RESULTS AND DISCUSSION

Phase transitions

The heat capacity of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$, as determined by adiabatic calorimetry, is shown as a function of temperature in Fig. 1 and the data have been deposited.¹³ The relevant lattice parameters from the single-crystal x-ray-diffraction study are presented in Figs. 2 and 3 and listed in Ref. 10.

There are three anomalous contributions to the heat capacity clearly seen in Fig. 1 and its inset. Thermodynamic data calculated for these anomalies, using the background heat capacity shown in Fig. 1, are summarized in Table I. The commensurate-incommensurate (C-IC) phase transition at $T = 346.20 \pm 0.25$ K and the incommensurate-normal (IC-N) phase transition at $T = 381.23 \pm 0.25$ K have been observed earlier⁶ by differential scanning calorimetry (DSC) (although the present measurements give both more accurate and more precise determinations of transition temperatures). The estimates of the entropy changes associated with these phase transitions given in the preliminary report⁶ are in a fair agreement with the more accurate results of the present work. In addition, the present results confirm the earlier supposition⁶ that the C-IC transition is first order (observed latent heat) while the IC-N phase transition is higher order (no latent heat). This is further confirmed from the lattice parameter results: the b and c axes both have steps at about 346 K, and all three axes are continuous with discontinuous changes of slope at about 382 K (Fig. 2).

The first-order transition at about 346 K is associated with a jump in the wave vector from $(0.258 \pm 0.002)c^*$ to

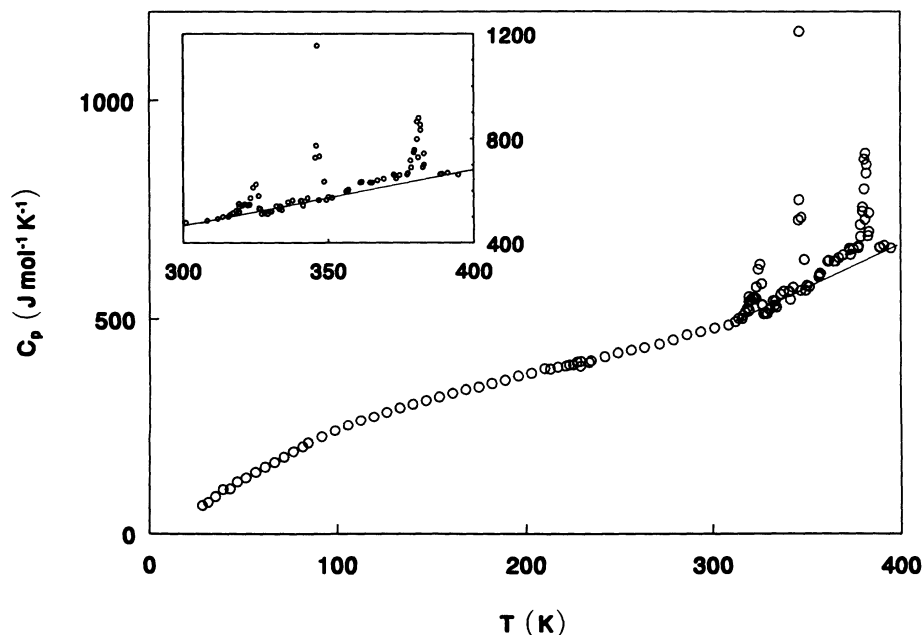


FIG. 1. Experimental heat capacities of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ as a function of temperature. The inset is an enlargement of the results over the phase transition region. The solid line represents the baseline heat capacity.

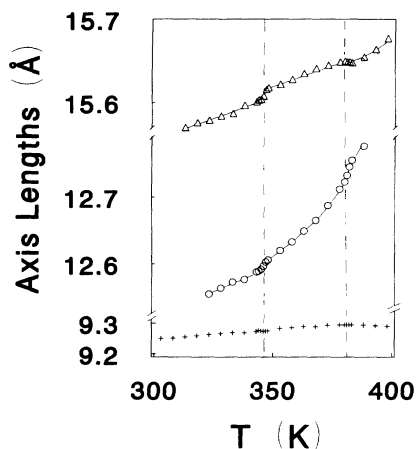


FIG. 2. The experimental values of the lattice parameters a (+) b (Δ), and c (\circ) of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ as functions of temperature. The vertical broken lines represent the temperatures of the phase transitions.

$c^*/3$, as verified in Fig. 4. The coexistence of commensurate and incommensurate phases in the figure is probably macroscopic, caused by a temperature gradient over the rather large crystal (*ca.* 0.4 mm) used for the experiment. Of interest in Fig. 4 is the second-order satellite visible at $l \approx 0.5$. Although the wave vector is irrational in the incommensurate phase, Fig. 4 shows the effective superposition of satellites for reflections $(h, k, l, 2)$ and $(h, k, l + 1, \bar{2})$. The (superimposed) second-order satellite reflection intensities were generally quite weak. Comparing absorption-, Lorentz-, and polarization-corrected data at 354 K, the most intense first-order satellite reflection, $(310\bar{1})$, was 7.3% as intense as the strongest primary reflection, (0400) , whereas the most intense superimposed second-order satellite reflections, $(0632)/$ $(064\bar{2})$, were together only 0.3% as intense.

The more accurate adiabatic calorimetric results confirm the preliminary finding, from differential scanning calorimetry:⁶ the ratio of entropy changes of the IC-N phase transition to the C-IC phase transition is unusually small. By accurate determination it was found here to be 1.5 ± 0.1 , which is much less than results obtained for compounds of the A_2BX_4 family: e.g., 61 for $[\text{N}(\text{CH}_3)_4]_2\text{CuCl}_4$,¹⁴ 175 for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$,¹⁵ 73 for K_2SeO_4 ,¹⁶ and 21 for Rb_2ZnCl_4 .¹⁶ The difference is mainly attributable to the larger value of $\Delta_{\text{tr}}S(\text{C-IC})$ for the present system, as $\Delta_{\text{tr}}S(\text{IC-N})$ is about the same for all systems mentioned above.

Our results also show an anomalous contribution to the

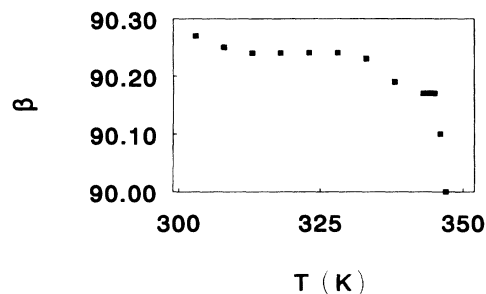


FIG. 3. The experimental values of the β angle (in degrees) of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ as a function of temperature.

heat capacity centered at around 325 K which was not observed in the earlier DSC scans.⁶ The thermal history of the sample appears to be important for the observation of this thermal anomaly: when the sample was cooled only to 319 K before heating in the adiabatic calorimetry experiment (see deposited table, runs 7 and 8), the anomaly at 325 K was less pronounced than if the sample had been cooled further (e.g., run 6 which had prior cooling to $T = 28$ K). However, x-ray analysis at room temperature following cooling to $T = 77$ K for 3 hours gave the same space group and lattice parameters as without this special heat treatment, so the origins of the 325-K thermal anomaly are not clear.

The full crystal structures, which have been determined at five different temperatures (294, 323, 354, 373, and 384 K) clearly show⁹ the differences between the lock-in structure, the incommensurate structure and the basic unmodulated structure.

Critical behavior analysis

In the preliminary study^{6,10} of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$, the temperature-dependent intensities (I) of several first-order satellites in the region of the IC-N phase transition were reported, with the untenable determination of significantly different critical exponents, 2β , for each. The exponents were determined from the relation $I \approx |T - T_i|^{2\beta}$ and subsequently are highly dependent on the chosen value of the critical temperature, T_i . As is apparent from Fig. 5, the residual intensity of satellite reflections from critical scattering at the IC-N phase transition makes the accurate measurement of T_i by direct analysis of integrated intensities difficult. However, the measurement of satellite reflection intensities away from the Bragg peak center and along c^* allowed¹⁷ an ac-

TABLE I. Thermodynamic changes associated with the phase transitions in $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$.

T_{tr} (K)	$\Delta_{\text{tr}}H$ (J mol^{-1})	$\Delta_{\text{tr}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$)
325.2 ± 0.5^a	580 ± 30	1.92 ± 0.09
346.20 ± 0.25	1260 ± 30	3.70 ± 0.09
381.23 ± 0.25	2020 ± 40	5.40 ± 0.10

^aTemperature of maximum in anomalous heat capacity; origins not known.

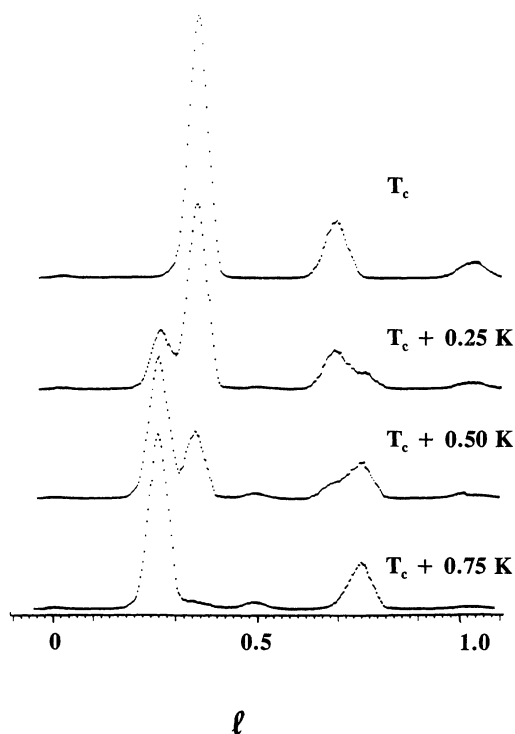


FIG. 4. X-ray-diffraction scans for $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ along $[31l]$ with l indexed with respect to the average structure. $T_c = 346$ K is the lock-in to the incommensurate phase transition temperature.

curate determination of T_i and the simultaneous determination of 2β . Specifically, the intensities around six reciprocal lattice points, centered on the strong first-order satellite reflection $(3, 1, 0 + \gamma)$ $[(3, 1, 0, 1)$ in four-indices notation] were measured and averaged. From the temperature of the maximum rate of change of intensity, T_i was estimated as 382.00 ± 0.25 K. The measurement and subsequent least-squares analysis of six first-order satellite reflections between 374 and 380 K, three of which are plotted in Fig. 5, gave $2\beta = 0.54 \pm 0.02$. Table II gives the independently determined exponents for the monitored satellites. The three curves of Fig. 5 show the universal

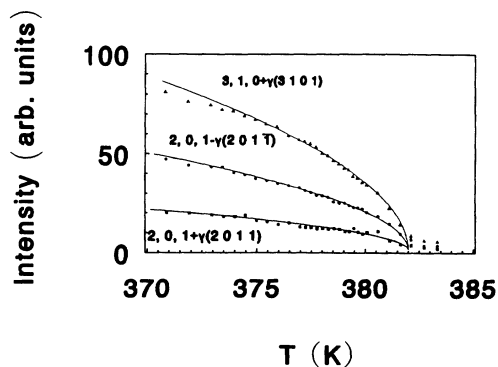


FIG. 5. The temperature-dependences of intensities of selected first-order satellite x-ray-diffraction reflections of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$. The solid lines correspond to fits with $T_i = 382.00$ K and the critical exponent $2\beta = 0.54$.

TABLE II. Critical exponents determined from first-order satellite reflections for $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ assuming $T_i = 382.00$ K.

Reflection	2β
$201\bar{1}$	0.51 ± 0.01
$\bar{2}0\bar{1}1$	0.54 ± 0.01
2011	0.47 ± 0.04
$20\bar{1}\bar{1}$	0.53 ± 0.03
3101	0.54 ± 0.01
$\bar{3}10\bar{1}$	0.54 ± 0.01

nature of the determined 2β value over the temperature range of the fit. The varying exponents determined in the preliminary study⁶ were probably caused by imprecision in determination of T_i and the attempt to fit the intensity data over too broad a temperature range (the entire range of the incommensurate phase).

The IC-N phase transition in $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ is a second-order incommensurate phase transition with a two-component order parameter of continuous symmetry. Its critical behavior should therefore be that of a three-dimensional XY model. It has been shown¹⁸ that the intensity of the first-order satellite reflections in the region of this transition would have the asymptotic temperature dependence $I \approx I_0 |T - T_i|^{2\beta}$, where a theory, based on the ϵ expansion of the 5th order, leads to¹⁹ $2\beta \approx 0.697 \pm 0.007$. It was found for the incommensurate phase transition in K_2SeO_4 that the critical exponent associated with the intensities of the first-order satellites is¹⁸ $2\beta = 0.75 \pm 0.05$, in reasonable agreement with the theory. However, our value, $2\beta = 0.54 \pm 0.02$, significantly contradicts the theoretical value. Similar contradiction was observed for other compounds of this family. For example, $2\beta = 0.55 \pm 0.03$ was found for the deuterated salt, $[\text{N}(\text{CD}_3)_4]_2\text{CuBr}_4$.²⁰ Possible causes of this discrepancy could include extinction effects, multiple scattering, and critical inelastic scattering.^{6,18} However, it is probable that the value of 2β reported here is an *effective* critical value reflecting fitting in a nonasymptotic region. Better resolution near the critical temperature could drastically change the value of 2β ; this also would permit a range-of-fit analysis to estimate the extent of the critical region in this salt.

The critical behavior of the heat capacity around the IC-N phase transition also has been investigated here using the calorimetric data obtained in the continuous heating mode. The logarithmic plot of the excess heat capacity, ΔC_p (given by the difference between the experimental heat capacity and the base line heat capacity shown in Fig. 1), as a function of the reduced temperature t , where $t = |T - T_p|$ is the absolute value of the difference between the temperature and the heat capacity peak temperature, T_p , is presented in Fig. 6. This plot is typical of several continuous heating runs carried out over the investigated temperature region except that T_p differs from run to run, depending on the heating rate. Typical data are given in the Appendix. (Because it depends on the heating rate, T_p also differs from the critical temperature accurately found with the adiabatic heat pulse method.)

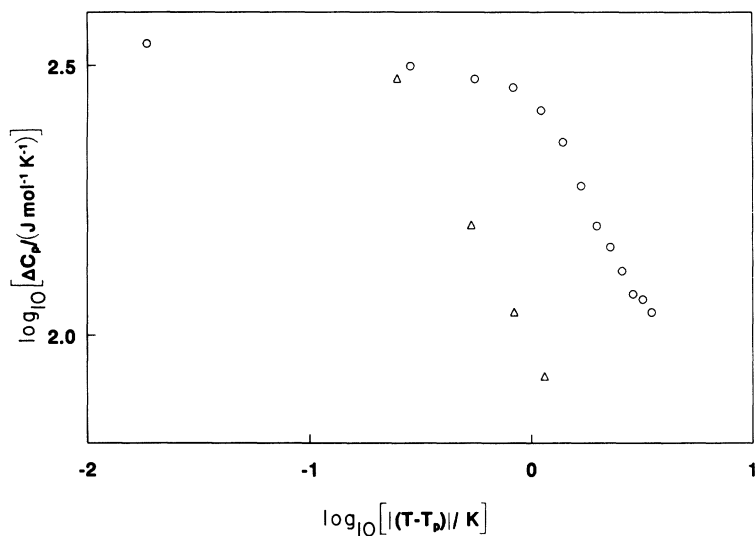


FIG. 6. The excess heat capacity ΔC_p as a function of reduced temperature, $|T - T_p|$, for $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$. Δ , $T > T_p$; \circ , $T < T_p$.

From Fig. 6 it can be seen that there is a tendency for the data on the low-temperature side of T_p to be linear in $\log_{10}|(T - T_p)|$ as T_p is approached, with the magnitude of the slope decreasing as $T \rightarrow T_p$. A linear least squares fit of this data in the temperature range $(T_p - T) < 1$ K gives a slope of -0.04 ± 0.01 . This suggests that the critical exponent, α' , is less than 0.04 (where $\Delta C_p \approx |(T - T_p)|^{-\alpha}$ for $T > T_p$ and $\Delta C_p \approx |(T - T_p)|^{-\alpha'}$ for $T < T_p$). Due to the rapid drop of the heat capacity above the peak temperature at the IC-N phase transition, we could not get sufficient data above T_p to make a conclusive statement about the critical behavior of the heat capacity above this phase transition. Similar analysis for $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ yielded¹⁵ $\alpha = \alpha' = 0.01$, which is consistent with our observation. However we think that better resolution near the critical temperature is needed in order to make more reliable statements about the value of α . A more complete analysis of the critical behavior would require more data in the proximity of the critical temperature and a fitting function that allows for regular contributions to the heat capacity of the phase transition and possibly for other singular terms. It is known, both from experiment and theory, that such terms generally must be present in the data analysis.²¹

IV. CONCLUSIONS

$[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ has been shown to undergo a first-order commensurate-incommensurate phase transition at 346 K, followed by a second-order incommensurate-normal transition at 381 K. The orders of the phase transitions, based on both calorimetric and lattice-parameter measurements, confirm the supposition of earlier preliminary investigations. Furthermore, $\Delta_{\text{r}}S$ has been accurately determined by adiabatic calorimetry for both these transitions, and the ratio of the entropy changes for the IC-N transition to the C-IC transition has been found to be unusually small. Analysis of the intensity of first-order satellite x-ray-diffraction reflections has been used to determine an effective critical exponent, β , for the IC-N transition. High-resolution calorimetric data, collected

in the region within 1 K of the incommensurate-normal transition, also gave an effective critical exponent (α'). However, further data, closer still to T_c , would be required in this system to permit range-of-fit analysis and produce firm conclusions concerning critical behavior.

ACKNOWLEDGMENTS

The authors thank R. Perry for assistance. The x-ray-diffraction facility was established in part through funds from NSF Grant No. CHE-8408407 and the Boeing Company. The calorimetric work was supported by the Natural Sciences and Engineering Research Council of Canada and The Killam Trustees.

APPENDIX

The excess heat capacity, ΔC_p , of $[\text{P}(\text{CH}_3)_4]_2\text{CuCl}_4$ as a function of temperature for a typical continuous heating run in the region of the incommensurate-normal phase transition; $T_p = 381.750$ K for this run.

T (K)	$\log_{10} (T - T_p) /K$	$\log_{10}[\Delta C_p / (\text{J K}^{-1} \text{mol}^{-1})]$
378.243	0.545	2.042
378.552	0.505	2.066
378.859	0.461	2.076
379.166	0.412	2.119
379.470	0.358	2.163
379.769	0.297	2.202
380.064	0.227	2.276
380.354	0.145	2.357
380.639	0.046	2.416
380.918	-0.080	2.459
381.192	-0.253	2.475
381.464	-0.544	2.499
381.731	-1.733	2.541
381.999	-0.604	2.476
382.287	-0.270	2.204
382.587	-0.077	2.043
382.898	0.060	1.924

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