Analysis of the specific-heat anomalies of K_2SeO_4 and Rb_2ZnCl_4 near the normal-incommensurate phase transition

Z. Y. Chen
Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
(Received 27 November 1989)

The specific-heat data in K_2SeO_4 and Rb_2ZnCl_4 are shown to be consistent with the expectation that normal-incommensurate phase transitions should belong to the universality class of the three-dimensional XY model.

For most displacive normal-incommensurate phase transitions, the symmetry mode in the high-temperature (disorder) phase is twofold;[1] the order parameter Φ associated with irreducible representation of the little cogroup of the modulation wave vector q is a complex variable, thus the $(n=2)$-component Landau-Ginzburg-Wilson Hamiltonian is appropriate near the normal-incommensurate transition temperature.[2] Most normal-incommensurate phase transitions then should belong to the universality class of the three-dimensional XY model, similar to the thermodynamic behavior of liquid helium near its λ point.[3] However, this expectation is not completely confirmed with exception to observations of the critical exponent β for the order parameter which can be obtained from, e.g., measurements of neutron-scattering intensity of the primary satellites.[4] The experimental value of β is insufficiently accurate,[4] nevertheless it seems to be consistent with theoretical results. On the other hand, different values of the critical exponent α for the specific heat C are reported experimentally.[5-9] These values are usually very different from the expected $\alpha \approx -0.0$ for the $d=3$ XY universality class. These experiments could be affected by defects and impurities,[10,11] but it is also likely that the discrepancy is caused by the fact that the experimental data is not analyzed correctly. In this Brief Report, the specific-heat data of dielectric crystals K_2SeO_4 and Rb_2ZnCl_4 (belonging to the A_2BX_4 family) are reanalyzed; these crystals undergo phase transitions from the normal to the incommensurate phase at $T_i(K_2SeO_4) = 128$ K and $T_i = (Rb_2ZnCl_4) = 304$ K. In particular, I shall restudy the specific-heat data reported by Atake and co-workers[5,6] using a crossover model that accounts for the crossover from singular critical behavior to regular classical behavior. When this procedure is done, it can be confirmed that the specific-heat data of Atake and co-workers can *indeed* be represented by the universality class of the three-dimensional XY model near the transition temperature.

Defining $\Delta T^* \propto (T - T_i)/T_i$, one should expect that the specific heat C contains two contributions near the transition temperature, the specific-heat anomaly[3]

$$\Delta C^{\pm} = \frac{A^{\pm}}{\alpha} |\Delta T^*|^{-\alpha}, \tag{1}$$

and an analytic function of temperature which is a combination of the background contribution and a fluctuation-induced analytic term.[12] In this equation, the "+" and "−" signs refer to approaching the transition temperature from above and below, respectively; A^+ and A^- are amplitudes, and α is the critical exponent. The theoretically determined value is $\alpha \approx -0.0$.[13] The universality hypothesis also predicts that the ratio A^+/A^- is a universal value. The field-theoretical value for this ratio is[14,15]

$$A^+/A^- = 1.03 \pm 0.01 . \tag{2}$$

Since α is very small, in practice, the value of α itself is less important and Eq. (1) can be written as

$$\Delta C^{\pm} = -A^{\pm} \ln |\Delta T^*| + \cdots , \tag{3}$$

after a suitable subtraction of the analytic part. In principle, the value of the ratio A^+/A^- can be determined from experimental data using representation (3); this is an important test for universal behavior of the normal-incommensurate phase transition.

To analyze experimental specific-heat data correctly using Eqs. (1) or (3), subtraction of the analytic contribution is quite crucial. Because of the smallness of the anomaly peak compared with the large background (see Fig. 1), a slightly different choice of the analytic background seems to affect the determination of the amplitude in Eq. (3) substantially. A complication also arises with incorporating correct crossover behavior to account for the regular behavior (a finite jump) far from the transition temperature which cannot be represented by simple power-law behavior in Eqs. (1) or (3). Instead of using Eqs. (1) or (3) to determine the exponent α and amplitudes $A^{\pm}$, a different approach to studying the experimental results is used in this Brief Report; the experimental data will be compared with a theoretical model for the thermodynamic properties, *with critical exponents and other universal features fixed* to the XY universality class. In particular, the crossover model for thermodynamic properties near the critical point proposed by Chen, Albright, and Sengers[16] is adopted here; this model was originally developed and was successfully used for thermodynamic properties of fluids near the vapor-liquid critical point (three-dimensional Ising systems). Here the three-dimensional XY universality exponents should be used in the model as described below. The original model is based on an approximation of the results from the renormalization-group approach to critical phenomena; hence, it is not an exact field-theoretical result. The applicability of this modification, especially to the specific-heat anomaly,

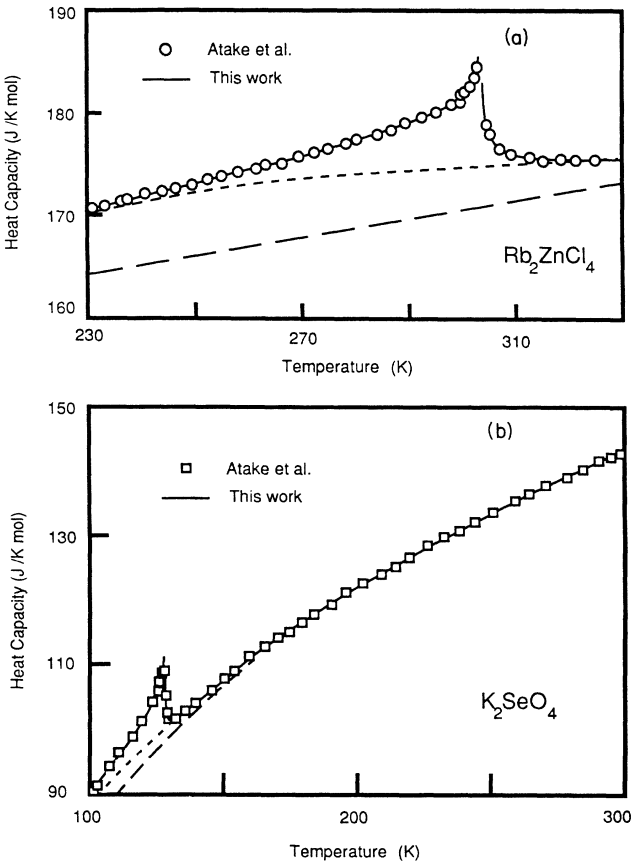

FIG. 1. Specific heat of (a) Rb_2ZnCl_4 and (b) K_2SeO_4 near the normal-incommensurate phase transition. The results produced from this work are represented by a solid curve going through the experimental data. The long-dashed curve is the background contribution determined in this work; the short-dashed curve is the background proposed in Refs. 6 and 7.

has to be verified near the critical point as described below.

The specific heat C and the Helmholtz-free-energy density A are made dimensionless with the aid of the critical temperature T_i and the molar gas constant R: $C^*=CT/RT_i, A^*=A/RT_i$. The Helmholtz free energy is written in the form

$$A^*(T,\Phi)=A_0^*(T)+\Delta A^*(T,\Phi), \tag{4}$$

where $A_0^*(T)$ is an analytic function representing background contributions and where ΔA^* incorporates the effect of the critical fluctuations. The fundamental equation for ΔA^* is[16]

$$\Delta A^*(T,\Phi)=\tfrac{1}{2}t|\Phi|^2\mathcal{Y}^{(2-1/\nu-\eta)/\omega}+\frac{u_0}{24}|\Phi|^4\mathcal{Y}^{(1-2\eta)/\omega}-\frac{n\nu}{2\alpha\bar{u}\Lambda}t^2(\mathcal{Y}^{-\alpha/\Delta}-1), \tag{5}$$

with the crossover function[17]

$$\mathcal{Y}=\left[\frac{1+(\bar{u}-1)\mathcal{Y}}{\bar{u}}\right]^{\omega}\left[1+\left(\frac{\Lambda}{\kappa}\right)^2\right]^{-\omega/2}, \tag{6}$$

and the approximation for the inverse of the correlation length[16]

$$\kappa^2=t\mathcal{Y}^{(2-1/\nu)/\omega}+\frac{u_0}{2}|\Phi|^2\mathcal{Y}^{(1-\eta)/\omega}. \tag{7}$$

Here $t=c_t(T-T_c)/T_c$ with c_t a proportionality constant, u_0 is the coupling constant for the $|\Phi|^4$ theory, $n(=2)$ is the dimensionality for the order parameter, $\bar{u}=u_0/u^*\Lambda$ with $u^*=0.4221$ the value of the fixed-point coupling constant for the XY model,[18] and with Λ the ultraviolet cutoff that is of the order of the inverse lattice constant. For the critical exponents of the XY model,[13] $\nu=0.669$, $\gamma=1.316$, $\omega=0.78$, $\alpha=3\nu-2=-0.007$, $\eta=2-\gamma/\nu=0.03288$, and $\Delta=\omega\nu=0.5218$. In the procedure of comparing the model with experiments, these critical exponents are *fixed* instead of fitted from experiments. The specific heat can be written in two terms $C=\Delta C+C_0(T)$. The background term $C_0(T)$, related to $A_0^*(T)$, is approximated by a truncated Taylor expansion:

$$C_0(T)/R=a_0+a_1T^*+a_2(T^*)^2+\cdots, \tag{8}$$

where $T^*=T/T_c$. Above the transition temperature, ΔC is calculated from

$$\Delta C^+(T)=-\frac{RT}{T_i}\frac{d^2}{d\Delta T^{*2}}\Delta A^*(T,0), \tag{9a}$$

and below the transition temperature ΔC is calculated from

$$\Delta C^-(T)=-\frac{RT}{T_i}\frac{d^2}{d\Delta T^{*2}}\Delta A^*[T,\Phi(T)], \tag{9b}$$

where $\Phi(T)$ is the spontaneous order parameter below T_i which is determined by requiring $\partial\Delta A^*/\partial\Phi|_{\Phi=\Phi(T)}=0$. In the limit $\kappa\gg\Lambda$, $\mathcal{Y}$ approaches unity and the critical fluctuations are unimportant; a jumplike specific-heat behavior is recovered and corresponds to the mean-field Landau-like behavior. In the limit $\kappa\ll\Lambda$, $\mathcal{Y}$ becomes proportional to $(\kappa/\Lambda)^{\omega}$ and the singular power-law behavior (1) is reproduced.[16] As mentioned above, the amplitude ratio A^+/A^- is an important test for specific heat. $A^+/A^-=1.0345$ produced from this model is in good agreement with theoretical results (2); hence, the model has correct critical behavior for specific heat. There are three independent nonuniversal constants c_t, $\bar{u}$, and Λ in Eqs. (5)–(7). The scaling constant c_t for the temperature field t is actually related to the overall magnitude of the specific-heat anomaly. Constants $\bar{u}$ and Λ govern the behavior of the crossover function $\mathcal{Y}$. The parameter $\bar{u}$ is related to the amplitude of the Wegner's correct-to-scaling series,[3] which is represented here in a "summed" form by the crossover function $\mathcal{Y}$.[12] The parameter Λ determines the temperature where the transition from critical to classical behavior takes place.[16]

A comparison of the model with experimental specific-heat data of Atake and co-workers for K_2SeO_4 between 230 and 330 K and Rb_2ZnCl_4 between 100 and 300 K has been conducted. System-dependent constants c_t, $\bar{u}$, and Λ are determined from a nonlinear fitting to the experimental data near the transition temperature. These constants are listed in Table I along with the fitted background pa-

TABLE I. Values of the system-dependent constants.

	Transition temperature	Scaling parameter	Crossover parameters		Background parameters			
	T_i	c_t	$\bar{u}$	Λ	a_0	a_1	a_2	a_3
K_2SeO_4	128.13 K	0.35996	0.48445	2.3731	0.0 (fixed)	17.456	−7.1145	1.1876
Rb_2ZnCl_4	304.16 K	0.40509	0.68755	2.2174	17.246	3.245	0 (fixed)	0 (fixed)

rameters. It was also found that the transition temperatures for K_2SeO_4 and Rb_2ZnCl_4 had to be chosen as listed in Table I in order to get a satisfactory representation for the experimental data near the transition temperature; these values can be compared with $T_i(K_2SeO_4)=127.7$ K and $T_i(Rb_2ZnCl_4)=303.2$ K reported originally by Atake and co-workers for the same data sets.[6,7] The average differences between the calculated and the experimental specific heat are 0.19% for K_2SeO_4 and 0.14% for Rb_2ZnCl_4. Figure 1 shows that the crossover model can indeed describe the specific-heat data from a singular peak up to a finite regular behavior. It is also interesting to compare the background contribution $C_0(T)$ in this work (represented by the long-dashed curve in Fig. 1) with the background contribution originally proposed by Atake and co-workers (the short-dashed curve).

In summary, using a theoretically-based representation one is able to represent the specific-heat data of Atake and co-workers[6,7] of K_2SeO_4 and Rb_2ZnCl_4 with experimental accuracy. Since the model used here reproduces universal features for the three-dimensional XY universality class, it can be concluded that the specific-heat data of Atake and co-workers is consistent with theoretical expectations. Because the model does not include the properties of the "lock-in" phase transition,[1] it cannot be extended to the incommensurate-to-commensurate phase-transition region. Furthermore, any contributions from the higher-harmonic[1] order parameter below the normal-incommensurate phase transition are ignored.

[1] J. C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987); T. Janssen and A. Janner, Adv. Phys. **36**, 519 (1987); R. Blinc and A. P. Levanyuk, *Incommensurate Phases in Dielectrics* (North-Holland, Amsterdam, 1986); V. L. Pokrovsky and A. L. Talapov, *Theory of Incommensurate Crystals* (Harwood, New York, 1984); P. Bak, Rep. Prog. Phys. **45**, 587 (1982); R. A. Cowley, Adv. Phys. **29**, 1 (1980).

[2] R. A. Cowley and A. D. Bruce, J. Phys. C **11**, 3577 (1978).

[3] See, e.g., *Phase Transition and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6; M. E. Fisher, in *Critical Phenomena,* edited by F. J. W. Hahne, Lecture Notes in Physics Vol. 186 (Springer-Verlag, Berlin, 1982).

[4] See, e.g., C. F. Majkrzak, J. D. Axe, and A. D. Bruce, Phys. Rev. B **22**, 5278 (1980); H. Mashiyama, J. Phys. Soc. Jpn. **49**, 2270 (1980).

[5] B. K. Chaudhuri, T. Atake, and H. Chihara, Solid State Commun. **38**, 927 (1981); T. Atake, K. Nomoto, B. K. Chaudhuri, and H. Chihara, J. Chem. Thermodyn. **15**, 339 (1983).

[6] B. K. Chaudhuri, K. Nomoto, T. Atake, and H. Chihara, Phys. Lett. **79A**, 361 (1980); T. Atake, K. Nomoto, B. K. Chaudhuri, and H. Chihara, J. Chem. Thermodyn. **15**, 389 (1983).

[7] A. Lopez-Echarri, M. J. Tello, and P. Gili, Solid State Commun. **36**, 1021 (1980); Ferroelectrics **26**, 695 (1980).

[8] I. N. Flerov, L. A. Kot, and A. I. Kriger, Fiz. Tverd. Tela (Leningrad) **24**, 1673 (1982) [Sov. Phys. Solid State **24**, 954 (1982)].

[9] K. Hamono, Y. Ikeda, T. Fujimoto, K. Ema, and S. Hirotsu, J. Phys. Soc. Jpn. **49**, 2278 (1980).

[10] M. E. Fisher, Phys. Rev. **176**, 257 (1968).

[11] A. P. Levanyuk and A. S. Sigov, *Defects and Structural Phase Transitions* (Gordon and Breach, New York, 1986).

[12] J. F. Nicoll and P. C. Albright, Phys. Rev. B **31**, 4576 (1985); **34**, 1991 (1986).

[13] J. C. LeGuillou and J. Zinn-Justin, J. Phys. Lett. **46**, L137 (1985).

[14] C. Bervillier, Phys. Rev. B **14**, 4964 (1976); **34**, 8141 (1986).

[15] V. Dohm, J. Low Temp. Phys. **69**, 51 (1987).

[16] Z. Y. Chen, P. C. Albright, and J. V. Sengers, Phys. Rev. A **41**, 3161 (1990); P. C. Albright, Z. Y. Chen, and J. V. Sengers, Phys. Rev. B **36**, 877 (1987).

[17] Z. Y. Chen, A. Abbaci, S. Tang, and J. V. Sengers (unpublished).

[18] J. C. LeGuillou and J. Zinn-Justin, Phys. Rev. Lett. **39**, 95 (1977).