

Thermodynamic study of commensurate-incommensurate phase transitions in Rb_2ZnCl_4

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We have performed simultaneous measurements of heat capacity and dielectric constant on a high-quality single crystal of Rb_2ZnCl_4 near the commensurate-incommensurate transition area. Maximum heat capacity is found to be at a higher temperature than the maximum dielectric constant, both for heating and cooling and in the area of a jump-wise change of the refractive index found earlier. When measuring heat capacity a peak-type anomaly was detected and the enthalpy of transition was measured. We compare our heat-capacity data with those for the powder samples and both sets with a phenomenological theory. We concluded that the Curie law for heat capacity predicted by the theory is observed in both cases with reasonable values for the Curie constant. We were unable to discriminate latent heat as in previous experiments with the powder sample; however, we estimated an upper limit for the latent heat by subtracting the contribution of specific heat to the enthalpy transition. The latent-heat value estimated both from the Clapeyron-Clausius formula and the phenomenological theory is qualitatively in accordance with the upper limit of this value found in our results. [S0163-1829(99)06321-3]

I. INTRODUCTION

In a continuous incommensurate-commensurate (lock-in) phase transition, thermodynamic quantities are expected to exhibit specific anomalies that are independent of the nature of the system.¹⁻³ Can these universal anomalies be observed experimentally? We will look for the answer for structurally incommensurate systems in three-dimensional solids. A simple model³ describes the commensurate-incommensurate transition as a spontaneous creation of the domain walls that repel each other and the formation of a regular structure of the walls, but first it is important to realize that no continuous incommensurate-commensurate transition can take place in these systems: long-range attractive forces^{4,5} must exist, which force the transition to be discontinuous. However, one may expect a temperature range (domainlike regime) where the repulsive force overcomes the attractive force, and thus universal anomalies should be observable. The role of the attractive force would then be reduced to a small range surrounding the transition point and would be responsible for its discontinuous character. Unfortunately, this regime is hard to observe experimentally.^{4,5} Moreover, experimental studies of the anomalies find a fundamental experimental difficulty in that the relaxation of the system towards equilibrium is so slow for temperatures close to the commensurate-incommensurate transition that it is practically impossible to observe the state of equilibrium studied by the theory (see, for instance, Ref. 6).

Still, at least one type of anomaly at the incommensurate-commensurate transition is quite well documented: the dielectric constant anomaly in incommensurate ferroelectrics, Rb_2ZnCl_4 , for example.⁷ However, even in this case the experimental data are not completely understood. The theory

predicts no anomaly in the commensurate phase while a broad anomaly is observed here on cooling⁸ (which can be explained by surviving nonequilibrium domain walls) and also on heating. Paradoxically, in the most perfect crystals the anomaly seen on heating is almost the same as that seen on cooling,⁹ while in less perfect crystals the anomaly seen on heating is much smaller, and thus, closer to what theory expects than in the high-quality crystals.

The specific heat has been studied to a much lesser extent, though, according to the theory, it has nearly the same form as the anomaly of the dielectric constant in the domainlike regime. The most detailed data have been published by Atake *et al.*¹⁰ who studied powder samples, as well as by earlier authors.¹¹ There are differences in some data of the two groups, probably because of a difference in the quality of the samples. In any case, no data on single crystals are known to us. At the same time, experiments with single crystals (interesting in and of themselves) have, moreover, an additional advantage: they permit simultaneous measurement of the dielectric constant. Such a possibility is crucial: the special importance of simultaneous measurements for the study of commensurate-incommensurate phase transition has been demonstrated by Novotná *et al.*¹² by measuring simultaneously the dielectric constant and the refractive index.

We attempted as well to provide an adequate theoretical discussion (Sec. II), both of our data and the previous data, because we feel the latter were not discussed satisfactorily. In Sec. III the experimental details and results are presented while the discussion is left for Sec. IV.

II. THEORY

Let us assume first that the commensurate-incommensurate transition is continuous. Under this assump-

tion, the domain-wall density will tend to zero at the phase-transition temperature ($T=T_{ic}$), that is, the surface energy of the wall is equal to $a_1(T_{ic}-T)$. The domain walls repel one another and the interaction energy has the following form:³ $W=a_2 \exp(-l/\kappa)$, where l is the distance between adjacent walls, κ is a quantity of the order of domain-wall width, and a_2 is a coefficient that does not depend appreciably on temperature in the area close to $T=T_{ic}$. In this area the thermodynamic potential per unit volume may be written as

$$\Phi = a_1(T_{ic}-T)l^{-1} + a_2 \exp\left(-\frac{l}{\kappa}\right)l^{-1}. \quad (1)$$

The most divergent part of the specific heat of the incommensurate phase is^{1,2,13}

$$C = -T \frac{\partial^2}{\partial T^2} (\Phi_e) \approx \frac{Ta_1}{\kappa} \left[\ln\left(\frac{a_2/a_1}{T-T_{ic}}\right) \right]^{-2} \frac{1}{T-T_{ic}} \approx \frac{C_1}{T-T_{ic}}, \quad (2)$$

where Φ_e stands for the equilibrium value of the thermodynamic potential (i.e., evaluated at the equilibrium interwall distance) and C_1 is the *Curie constant*, which can be estimated by evaluating the logarithm at some temperature (T_1) within the interval of an (approximate) fulfillment of the Curie law, say, in the middle of this interval,

$$C_1 = T_{ic} \frac{a_1}{\kappa} \left(\ln \frac{a_2/a_1}{T_1 - T_{ic}} \right)^{-2}. \quad (3)$$

The Landau-like theory² shows that a_2/a_1 is in the order of magnitude of $T_1 - T_{ic}$ and, therefore, the value of the squared logarithm is hardly more than ten.

The anomalous part of electric susceptibility of the incommensurate phase is¹⁴

$$\chi = \frac{\partial P}{\partial E} = \frac{P_s^2 \kappa / a_1}{T - T_{ic}} = \frac{C_2}{T - T_{ic}}, \quad (4)$$

where C_2 is the *Curie constant*.

By combining Eqs. (3) and (4), one gets

$$C_1 C_2 = TP_s^2 \left[\ln\left(\frac{a_2/a_1}{T_1 - T_{ic}}\right) \right]^{-2}. \quad (5)$$

We will use this formula to discuss the experimental data. It can be obtained, of course, from the Landau-like theory but as a result of fairly tedious calculations.

As the commensurate-incommensurate transition is discontinuous, one may be interested in the latent heat of the transition. The simplest way is to apply the Clapeyron-Clausius formula, which is valid for any discontinuous transition with a change in the spontaneous polarization (from P_s to zero in our case):

$$\frac{dT_{loc}}{dE} = \frac{-TP_s}{Q}, \quad (6)$$

where T_{loc} is the transition temperature and Q is the latent heat of transition.

An alternative way is to estimate the latent heat from the above theory taking into account the domain-wall attraction. Unfortunately, this is not easy. The fact is that there is no universal formula for the attractive term of domain-wall en-

ergy, not to mention that there are different contributions to this energy.⁴ To have at least an approximate idea of what results from the theory, considering the domain-wall interactions, we shall consider the case of the strongest attraction (proper ferroelectrics) mainly because no new parameters are to be introduced in this case. We also keep in mind that for interwall distances comparable with the domain-wall width some other contributions provide comparable energies.⁴ In other words, we consider the thermodynamic potential

$$\Phi = a_1(T_{ic}-T)l^{-1} + a_2 \exp\left(-\frac{l}{\kappa}\right)l^{-1} - \frac{T}{4\pi}l^{-3}. \quad (7)$$

At $T=T_{loc}$ the thermodynamic potential is equal to zero. From this condition together with minimization of the thermodynamic potential with respect to l we obtain

$$l_{01} = \kappa \ln\left(\frac{a_2/a_1}{2(T_{ic}-T_{loc})}\right) \quad (8)$$

for $l_{01} \gg \kappa$.

As the value of the logarithm is never very high in practice, one sees that l_{01} is never very different from κ , as was already mentioned in Ref. 4. To estimate the change of entropy due to transition into the incommensurate phase one can differentiate Eq. (7) with respect to T and then use Eq. (8). By simply keeping the most important term, it is possible to know that the entropy is around $a_1 l_{01}^{-1}$. Using then Eq. (4), the latent heat of transition is

$$Q = T_{loc} \frac{P_s^2}{C_2} \left[\ln\left(\frac{a_2/a_1}{2(T_{ic}-T_{loc})}\right) \right]^{-1}. \quad (9)$$

We will use this formula in a further discussion, bearing in mind, of course, its approximate character.

The logarithm can be estimated, in theory, if one knows the period of the incommensurate phase at $T=T_{loc}$. In our case this period is equal to $6l$. The Landau-like theory of the incommensurate phase² allows us to relate coefficient k with the wave vector of the incommensurate phase near the normal-incommensurate transition (q_0). One gets

$$\kappa = \frac{2}{3\pi} q_0. \quad (10)$$

Thus, from Eqs. (8) and (10) one finds

$$q_{loc} = \frac{\pi}{3l_{01}} = \frac{\pi^2}{2} q_0 \left[\ln\left(\frac{a_2/a_1}{2(T_{ic}-T_{loc})}\right) \right]^{-1}. \quad (11)$$

Data on q_{loc}/q_0 in Rb_2ZnCl_4 vary for different authors (see Refs. 15–18) and indicate an important thermal hysteresis, suggesting a strong influence of the sample quality and experimental conditions. Most data range between $\frac{1}{2}$ and $\frac{1}{6}$. This means that the latent heat estimated according to Eq. (9) is at least one order of magnitude lower than the prelogarithmic factor in this equation.

Finally, the Landau-like theory also provides information about the values of C_1 and C_2 . From Eq. (28) of Ref. 2 one can see that

$$C_2 \sim T_i - T_{ic}, \quad (12)$$

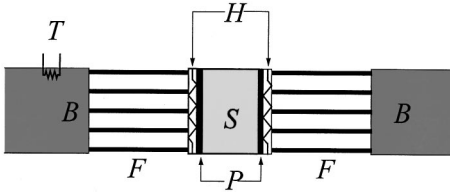


FIG. 1. Outline of the calorimetric cell. (S) represents the sample, (B) is a large thermal capacity block whose temperature is measured with a platinum resistance thermometer (T). Two fluxmeters (F) connect both block and sample and provide thermal conduction between them. There exist two heaters (H) and two silver plates (P) to provide electric measurements. Heat can only flow from sample to block through the fluxmeters.

where T_i is the temperature of the normal-incommensurate phase transition. On the other hand,

$$C_1 \sim C_2 \Delta C, \quad (13)$$

where ΔC is the difference between the specific heat of the commensurate and the normal phase. The latter is conventionally estimated (see, e.g., Ref. 19) as

$$\Delta C \sim \frac{k_B}{d^3} \quad (14)$$

for order-disorder type transitions and as

$$\Delta C \sim \frac{k_B}{d^3} \frac{T_i}{T_{at}} \quad (15)$$

for displacive system. Here k_B is the Boltzmann constant, d is the interatomic distance, and T_{at} is a temperature of the order of magnitude of the atomic energy. It is advisable to introduce a dimensionless specific heat normalizing it to $R/v \sim k_B/d^3$, where R is the ideal gas constant and v is the molar volume. Then, for the corresponding Curie constant one has

$$\tilde{C}_1 \sim C_2 \quad (16)$$

for order-disorder systems and

$$\tilde{C}_1 \sim C_2 \frac{T_i}{T_{at}} \quad (17)$$

for the displacive systems. One sees that the anomaly of the (normalized) heat capacity is much stronger than the anomaly of the dielectric susceptibility in order-disorder systems and is much weaker in the displacive ones.

III. EXPERIMENT AND RESULTS

To study the heat capacity near the lock-in transition in Rb_2ZnCl_4 single crystals we used a high-precision calorimeter,²⁰ useful for the simultaneous measurement of specific heat and dielectric permittivity for both cooling and heating runs. The calorimeter consists (see Fig. 1) of a large calorimetric block, whose mass makes it a thermal reservoir, and two fluxmeters, which both form sets of 96 thermocouples thermally constructed in parallel and electrically in series. One junction of the thermocouples is fixed to the

block (outer junction) while the other one is fixed to an anodized silver plane plate. The sample is kept between two electric heaters (allowing thermal excitation of the sample) and two silver electrodes, which allows simultaneous measurement of the dielectric permittivity by an ESISP5240 capacitance bridge.²¹ Special care is taken in conserving the axial symmetry of the assembly. By creating a high vacuum (10^{-5} mbar) inside the calorimetric vessel and providing it with radiation shields the main objective of the assembly is obtained, that is, *any heat flux flowing from the block to the sample must cross the fluxmeters*. The heat capacity of the sample is measured by dissipation on the heaters. When a stationary state is reached, the power is cut off. The study of the relaxation process towards equilibrium gives us the heat capacity.²²

A purified sample of rubidium tetrachlorozincate (Rb_2ZnCl_4) was placed in the calorimeter. The sample had a 289-mg mass (0.764 mmol) with a 25-mm² cross section and a width of 3.14 mm along the ferroelectric axis. Above $T_i = 305$ K the Rb_2ZnCl_4 single crystal presents an orthorhombic pseudohexagonal ($Pnma$) phase;²³ it is paraelectric and paraelastic. At T_i , a continuous phase transition transforms it into an incommensurate crystal with a modulation wave vector close to one-third of a^* . Finally, at $T_{ic} = 195$ K, the crystal phase locks into a commensurate phase that is again orthorhombic ($Pna2_1$) but ferroelectric along the c axis and with tripled unit cell.

The sample was cooled from the *para* phase to a temperature of 200 K in the incommensurate phase. Then, at a rate of 0.1 K h⁻¹, the sample was cooled to the commensurate phase while measuring the specific heat and dielectric permittivity. After cooling it to 100 K, the sample was heated again to the incommensurate phase while measuring the specific heat and dielectric permittivity.

Simultaneous data of specific heat (upper graph) and dielectric permittivity (lower graph) are presented in Fig. 2. Dielectric permittivity data show a large peak value and low thermal hysteresis of the temperature of maximum permittivity, $T_{\max}^c = 194.3$ K and $T_{\max}^h = 194.8$ K, thus the quality of the crystal can be described as purified in the sense of Ref. 24. On the other hand, as shown⁷ before, permittivity data obey the Curie law in a range of a few Kelvin above T_{ic} . This is in accordance with theoretical predictions. Our data find $T_{ic} = 194.5$ K and $4\pi C_2 = 68$ K, where C_2 is the Curie constant defined in Eq. (4) being close to the value found in Ref. 25.

In Fig. 2, data of specific heat for a cooling and heating process are presented. The temperatures of maximum specific heat are $T_{\max}^c = 194.6$ K and $T_{\max}^h = 194.9$ K. A small tail on the left-hand side of the anomaly is clearly seen on the plot; this tail shows the nonequilibrium nature of the specific-heat value in the commensurate phase. The enthalpy of transition, represented by the area of the anomaly, is found to be 2.7 J mol⁻¹ (cooling) and 2.8 J mol⁻¹ (heating). From the experimental data, the existence of latent heat is not clear as the specific heat increases only by 10% and the peak anomaly is presented over a temperature range of 1 K. We deal with this point further in Sec. IV.

According to the thermodynamic theory reviewed in Sec. II, the specific heat of the incommensurate phase should become $(T - T_{ic})^{-1}$ near the phase transition, where the do-

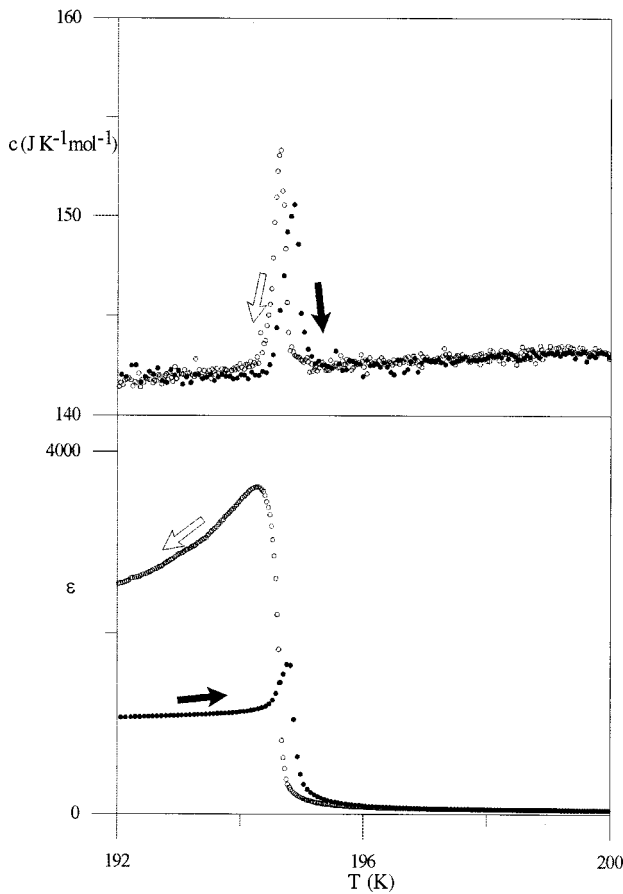


FIG. 2. Data of specific heat (upper graph) and dielectric permittivity (lower graph) for cooling (open circles) and heating (solid circles) runs. Measurements are simultaneous.

mainlike regime is possible [see Eq. (2)]. A semiquantitative experimental proof of this equation seems difficult to achieve due to the experimental noise and the low specific-heat excess value during the phase transformation. We point out that the dielectric permittivity changes as much as two orders of magnitude while specific heat does so only by 10%. Figure 3 shows the data for inverse excess specific heat, in ideal-gas constant units, versus temperature, along with the best fit to a straight line. We experimentally determine the Curie constant as $\tilde{C}_1 = 11 \times 10^{-3}$ K (cooling) and $\tilde{C}_1 = 19 \times 10^{-3}$ K (heating). This figure is a proof of the qualitative fulfillment of Eq. (2). In Sec. IV we discuss the validity of the fitting.

The experimental data are better presented with both permittivity and specific heat plotted simultaneously as in Fig. 4 for the cooling branch. The fact that measurements for both were taken simultaneously allows us to highlight some points. First, we show that the Curie laws for specific heat and dielectric permittivity are simultaneously satisfied until T_1 (see Fig. 4) is reached. Second, the maxima for specific heat and permittivity are shifted: the specific-heat maximum (T_2) nearly coincides with the inflection point of permittivity, while the permittivity maximum (T_3) nearly coincides with the end point of the specific-heat anomaly. As a whole, qualitatively, the permittivity behaves as the derivative of the specific heat during the anomaly. The results seem quite similar to the simultaneous measurement of refractive index and permittivity obtained by Novotná *et al.* (see Ref. 12).

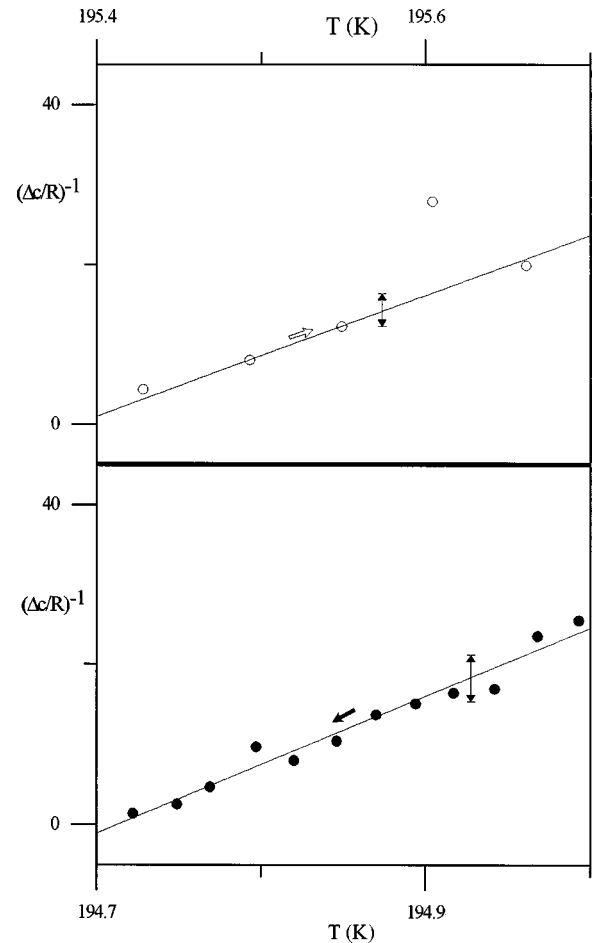


FIG. 3. Fit of the specific-heat excess to the Curie-Weiss law. Calculated Curie temperatures are 194.7 K (cooling) and 195.3 K (heating). Curie constants are 11×10^{-3} K (cooling) and 19×10^{-3} K (heating). Adjusted data correspond to the low kink observed on the right side of the anomaly in Fig. 2.

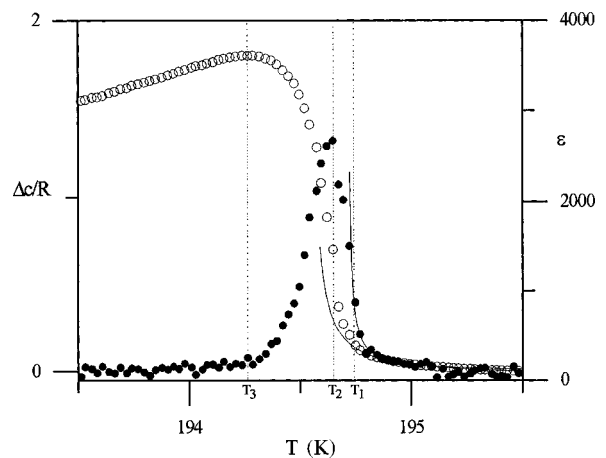


FIG. 4. Simultaneous analysis of the relative excess of specific heat (left axis, solid circles) and the dielectric permittivity (right axis, open circles). The Curie laws for both magnitudes are also shown. Curie laws are simultaneously satisfied until T_1 is reached. Maximum specific-heat data (T_2) coincides with the inflection point of the permittivity while maximum permittivity (T_3) coincides with the end point of specific-heat anomaly.

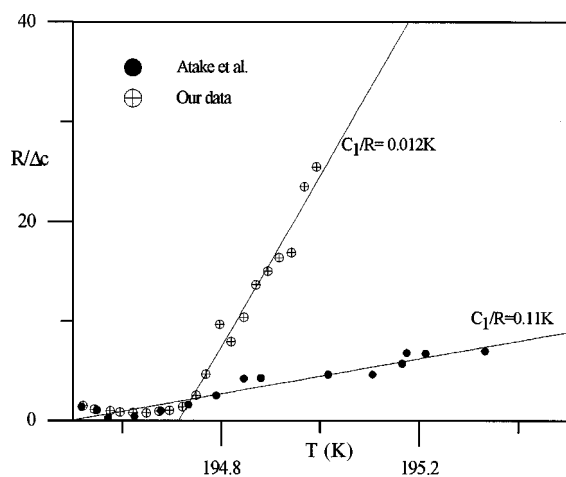


FIG. 5. Inverse specific-heat data (in ideal-gas constant units) from Atake *et al.* (Ref. 10) and from our data. The values of “Curie constants” C_1 are given in the drawing. Temperature has been arbitrarily shifted so as to get the same critical temperature for both experiments.

IV. DISCUSSION

The maximum excess of heat capacity observed in Ref. 10 is somewhat higher than in our experiments ($29 \text{ J mol}^{-1} \text{ K}^{-1}$ and $11 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively), however, our data are in accordance with Ref. 11, which is $12 \text{ J mol}^{-1} \text{ K}^{-1}$. More significant is the difference of the anomaly in the commensurate phase: it is much smaller in our sample than in Refs. 10 and 11. On the other hand, we found the Curie constant from Ref. 10 data (see Fig. 5) and it is one order of magnitude higher than in our case; the value of \tilde{C}_1 for the data by Atake *et al.*¹⁰ is about 10^{-1} K . This may prove that the quality of our single crystal, which is quite high, as has been mentioned before, is still lower than that of the powdered samples. On the other hand, the Curie constant C_2 is about 5 in our sample and similar values are found by other authors.²⁵ This does not seem to depend so much on the quality of the crystal and it seems reasonable to expect that it will be of the same order of magnitude for the microcrystals composing the powder. According to Eq. (17), the ratio of the two constants is expected to be 10^{-2} – 10^{-3} , i.e., the experimental ratio is close to typical values for displacive systems.

Let us now check the validity of Eq. (5). Using the same experimental data one obtains, for the left side of the equation, $4 \times 10^3 \text{ J K m}^{-3}$, and for the prelogarithmic factor on the right side, $2 \times 10^4 \text{ J K m}^{-3}$. One sees that, with the logarithm of the order of magnitude of the unity, the experimental data are in accordance with the equation. Thus, one may suppose that the Curie law for the specific heat observed both in Ref. 10 and in this work is the one predicted by the theory, concluding that the Curie constant for the specific heat is more sensitive to the sample quality than the Curie constant for the susceptibility.

The main problem in the interpretation both of our data and those obtained in Refs. 10 and 11 lies with the latent heat of transition. In short, the peak area in Fig. 3 does not strictly represent the *latent heat*, but rather the *enthalpy of transition*. It is the *latent heat* (an unknown part of the enthalpy transition) that enters the Clapeyron-Clausius formula; however,

in Ref. 10 Atake *et al.* used the *enthalpy of transition* (6.2 J mol^{-1}) to compare it with the Clapeyron-Clausius formula. As such, the accordance claimed in Ref. 10 is far from being natural and it is not conclusive; they implicitly assume that the latent heat is the leading term in the enthalpy of transition and neglect the contribution of excess specific heat. A more detailed discussion would be desirable. As a first approach to the value of the latent heat, one may think of subtracting the contribution of the Curie-like divergence in the heat capacity. In doing so, we find that this contribution may represent as much as 50% of the total enthalpy transition given by Atake *et al.* On the other hand, this contribution represents only about 15% of the enthalpy transition in our data; the difference should be ascribed to the characteristics of the samples. Thus, the latent heat of the transition should be lowered to 2 – 3 J mol^{-1} .

It is important to emphasize that this is an upper limit of the latent heat rather than the value itself. Indeed, it also includes a contribution from the temperature range within the incommensurate phase where attraction becomes important (Sec. I). This contribution strongly depends on the temperature width of the range and is hardly reliable within the existing theory. The fact that the above latent heat is in accordance with the Clapeyron-Clausius formula might indicate that the contribution of this range is not decisive.

The latent-heat value calculated from the Clapeyron-Clausius formula contradicts neither the estimation due to Eq. (9) nor our estimated latent heat described above. Indeed, the prelogarithmic factor on the right side of this equation is about 100 J mol^{-1} and a logarithmic value of approximately ten seems quite reasonable, even if the latent heat may be somewhat overestimated by the formula. Of course, one should not take the accordance too seriously because the value of dT_{loc}/dE was measured²⁶ for samples with relatively poor quality: the temperature hysteresis was about 2.8 K, while in the best single crystals it was about 0.2 K. It would be interesting to measure dT_{loc}/dE for high-quality single crystals.

Thus, we may conclude that, first, the Curie law for heat capacity is approximately fulfilled both for single crystals and powdered crystals and the value of the Curie constant is in accordance with the theory. Second, the phase transition is at least partially smeared and discrimination between latent heat and specific heat excess seems difficult. This may seem surprising as the values of latent heat obtained by the Clausius-Clapeyron formula and the phenomenological theory are found to be high enough to be observed. We are able to obtain an upper limit for the latent heat, which is in qualitative accordance with theoretical predictions.

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