

Evidence of latent heat in Rb_2ZnCl_4 commensurate-incommensurate phase transition

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The commensurate-incommensurate phase of a Rb_2ZnCl_4 crystal was studied using a conduction calorimeter. By identifying the contribution of specific heat to transition enthalpy it was possible to show, for the first time in a compound of this type, transition latent heat. It was estimated to be $Q = 2.3 \text{ J mol}^{-1}$. The result was compared with theoretical predictions for a domain wall model having repulsive-attractive interaction, obtaining satisfactory results for the first time. The same analysis was made in normal-incommensurate phase transition and no latent heat was observed as expected.

I. INTRODUCTION

The study of commensurate-incommensurate phase transitions in crystal systems has been of major interest for over a decade. It has been theoretically established that in a commensurate-incommensurate transition, continuity of physical anomalies takes place independently of the nature of the system [1–3]. To establish this phase transition the study must comprise the normal-incommensurate phase transition always present at higher temperature. In so doing, the mathematical framework of the commensurate-incommensurate phase transition becomes considerably more complicated [2]. Nevertheless, a simpler analysis can serve the purpose, provided that attention be focused solely on the commensurate-incommensurate transition. Generally, this transition can be understood from the spontaneous appearance of domain walls in a monodomain structure; the interacting force between domain walls is a determining factor when describing properties of the transition: if the interaction was purely repulsive, the transition would be continuous. However, there are always attraction forces in ferroelectric structural transitions that cause the transition to be discontinuous [4, 5].

Repulsion forces are dominant in a wide range of temperatures above transition temperature and yield theoretical expressions on the divergences for dielectric susceptibility and specific heat, as in reference [2]. Experimentally, the anomaly of the dielectric constant was analyzed within this formalism by Levstik *et al.* [6], ascertaining that it diverged from the $(T - T_{ic})^{-1}$ law precisely as set forth theoretically. The specific heat peak was described as manifestation of the transition's discontinuous nature, but lately [7] there has been proof that its divergence in the incommensurate phase matches, as well, that which is expected from the repulsion potential. Other properties, such as the misfit parameter [8–10], or birefringence [11], display certain characteristics implying a discontinuous transition and indicate that, within a

given temperature range approaching transition temperature, the presence of attractive forces is not to be discarded. Within this temperature range, corresponding to the final part of the permittivity peak and specific heat, predictions in the repulsion model do not hold true [7].

Calorimeter measurements near the transition temperature lead to difficulties in discriminating the enthalpy variation due to latent heat from that owing to the excess specific heat integral over temperature. This problem becomes more acute in cases where latent heat is very small, such as in the commensurate-incommensurate phase transition. Thus, although the discontinuous character of the transition has been known for over a decade, calorimetric measurements have not yielded clear evidence of latent heat. On one hand Atake *et al.* [12] used the integral of the anomaly of specific heat in the Clausius-Clapeyron formula, implicitly assuming that it meant latent heat. On the other, Zhu *et al.* [13] estimated latent heat of *barium sodium niobate* (BSN) from DSC measurements. In neither of the two instances were the two previous contributions taken into account.

Nonetheless, theoretical analysis of the phase transition shows that specific heat must be subject to an anomaly evinced by a sharp peak, inasmuch as it diverges in accordance with Curie's law, with a relatively small constant proportionality (three-four orders of magnitude less than permittivity in the same transition phase). Therefore, the specific heat anomaly is detectable only within a temperature range nearing T_{ic} (approximately 1K). In contrast, estimations in the Clapeyron formula indicate latent heat in the order of a few joules per mole [14]. In consequence, it becomes necessary to analyze both contributions.

In the present paper a conduction calorimeter has been used which can measure specific heat and also serves as a DTA apparatus of great sensitivity inasmuch as the sensor is made up of 96 thermocouples. The theory set forth previously allows for discrimination between the two contributions listed. This technique was applied in establishing latent heat for the commensurate-incommensurate transition in the Rb_2ZnCl_4 crystal. To cross check the method, the same procedure was used in the normal-incommensurate phase transition, which is a continuous transition where the enthalpy variation results solely

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from specific heat.

II. EXPERIMENTAL

A purified sample of *rubidium tetrachlorozincate* (Rb_2ZnCl_4) was placed in a conduction calorimeter. The sample has 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; it is paraelectric. At T_i , a continuous phase transition transforms it into an incommensurate crystal with a modulation wave vector close to one third of \mathbf{a}^* . Finally, at $T_{ic} = 195$ K, the crystal phase locks into a commensurate phase which is again orthorhombic ($Pna2_1$) but ferroelectric along the c axis and with triple unit cell [15]. Rb_2ZnCl_4 has been widely chosen as a test for the theoretical description of both the commensurate-incommensurate phase transition and the normal-incommensurate phase transition.

The conduction calorimeter has been described elsewhere [16]. Briefly, it consists of a large calorimetric block whose mass makes it a thermal reservoir. Two fluxmeters which both form a set 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 which has an electric heater of negligible thermal capacity. The sample is kept between both heaters (allowing thermal excitation of the sample). Special care is taken in conserving the axial symmetry of the assembly. By making high vacuum (10^{-5} mbar) inside the calorimetric vessel and providing it with radiation shields the main objective of the assembly is obtained; any heat flux flowing from the block to the sample must cross the fluxmeters. The heat capacity of the sample is measured by dissipating the same power on the heaters. When a stationary state is reached the power is cut off. The value of the thermal capacity is obtained by integrating the electromotive force given by the fluxmeters during the relaxation to equilibrium state [17].

The system can also be used as a *differential thermal analyzer* (DTA) of great sensitivity when temperature of the block is modified at constant rate and no dissipation whatsoever is applied to the heaters. In such case, the measured thermoelectromotive force, E is proportional to heat flow, ϕ (the factor being determined previously by calibration), and ϕ is related to sample enthalpy variation.

Theoretically, well away from transition point the heat flux should be proportional[18] to temperature change rate, and heat capacity of sample and its surroundings (fluxmeters, silver electrode and heaters). That is:

$$\phi_0 = (C_s + C_0) \frac{dT}{dt}. \quad (1)$$

Here C_s is sample heat capacity and C_0 represents the heat capacity of surroundings. This value can be obtained by giving sample heat capacity and calibrating C_0 as we will show in Sec. III. The existence of latent heat can be shown by measuring ϕ and comparing with ϕ_0 . The latent heat will be obtained as:

$$Q = \int (\phi - \phi_0) dt. \quad (2)$$

where the integral covers the transition point. We will show that this difference is negligible for a continuous phase transition as ϕ and ϕ_0 match each other. The physical meaning of ϕ_0 is then, the heat flow which would have been obtained had there been no latent heat.

The Rb_2ZnCl_4 sample was set in the conduction calorimeter and cooled in the paraelectric phase to 100 K temperature. Afterwards, the sample was heated at a constant rate of 2K h^{-1} to room temperature whilst fluxmeter thermoelectromotive force signals were registered as functions of temperature. The thermoelectromotive force was recorded by a *Keithley K182* nanovoltmeter. At 190 K and 200 K the calorimeter was calibrated [16] in order to convert the fluxmeter signal into heat flow. A similar experiment was performed near the normal-incommensurate phase transition.

III. RESULTS

In figure 1, fluxmeter signals near the normal-incommensurate phase are represented by full circles. In this figure, the thermoelectromotive force has been converted into heat flow and, then, divided by sample mole number. The anomaly in the signal is due to variation of transition enthalpy. To establish the existence of latent heat, we need to compute the value of ϕ_0 : we proceeded as follows. Let us consider the values of heat flux and sample heat capacity (the latter being measured in the same calorimeter and sample, and shown in the small graph in figure 1) at two temperatures distant from phase transition point, for example at 302 K and 305 K where the measured ϕ should be equal to ϕ_0 . From equation (1), and being dT/dt known, we determine C_0 at these temperatures and then we are able to determine C_0 dependency with respect to temperature as it is certainly a smooth function of temperature and should be assumed to be linear. C_0 being known, and using values for specific heat measured in transition, ϕ_0 can be calculated as a function of temperature by invoking again equation (1). This function represents the enthalpy variation due to excess specific heat and is represented in figure 1 by a line of open circles. As can be seen, measured heat flow and what is expected due to excess specific heat are exact matches in form and value. Therefore the only contribution to transition enthalpy is excess specific heat, and resulting latent heat is zero (within the equipment's

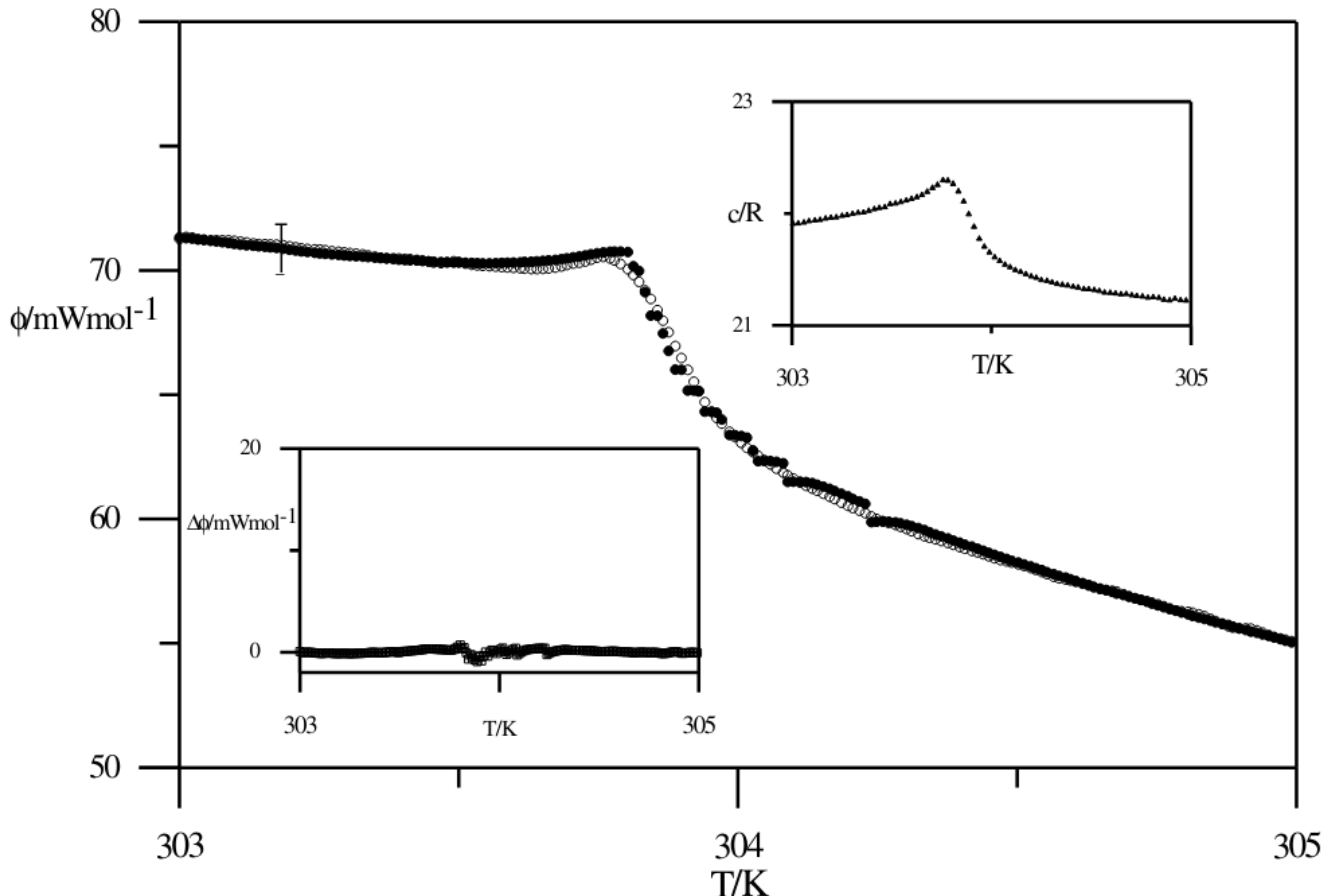


FIG. 1. Measured heat flux (full circle) and deduced background contribution (open circle) from specific heat data (inserted graph) in the neighbourhood of normal-incommensurate phase transition. The specific heat was measured in the same calorimeter on the same sample. The heat capacity contribution (see equation (1)) fully explains the anomaly observed. Thus, no latent heat is observed within experiment resolution in agreement with the $3d$ - XY universality class of this phase transition.

resolution). This is the result to be expected for this transition which belongs in universality class $3 - dXY$.

In figure 2 the same analysis is shown, but near the commensurate-incommensurate transition phase. Measured heat flow, ϕ , which includes contributions from latent heat and specific heat, is represented by full circles. Heat flow ϕ_0 , calculated from specific heat data, are in open circles. In that figure the right axis reflects $\phi - \phi_0$ in open squares. These data show that enthalpy variation cannot be explained solely by way of the specific heat contribution and, therefore, show the presence of latent heat. The integral of equation (2) is evaluated in $Q = 2.3 \text{ J mol}^{-1}$. Also significant is the apparent double peak, which cannot be subject to interpretation in terms of specific heat anomaly and could be due to some kinetic process in transition.

IV. DISCUSSION

The greatest difficulty in identifying latent heat with the peak zone in figure 2 lies in the peak's width. Ideally, latent heat would be observed only at a single temperature and the peak should tend towards a Dirac delta function if represented as a function of temperature (as a function of time it would always be of finite width); even then a width of some 0.2 K is observed. In this regard it should be noted that given $dT/dt = 2 \text{ K h}^{-1}$, the 0.2 K span means a six-minute interval, which is the order of magnitude of relaxation of the calorimeter. Having understood the peak's width, the shape of the anomaly, with its double peak, is quite different from that expected of a heat-specific anomaly, so that this area represents a near approximation of transition latent heat value and, at any rate, proof of its existence. Of course, the specific heat data may be affected, to some extent, by the existence of latent heat but the difference between figure 1 and figure 2 is significant.

On the other hand, the difficulty in distinguishing la-

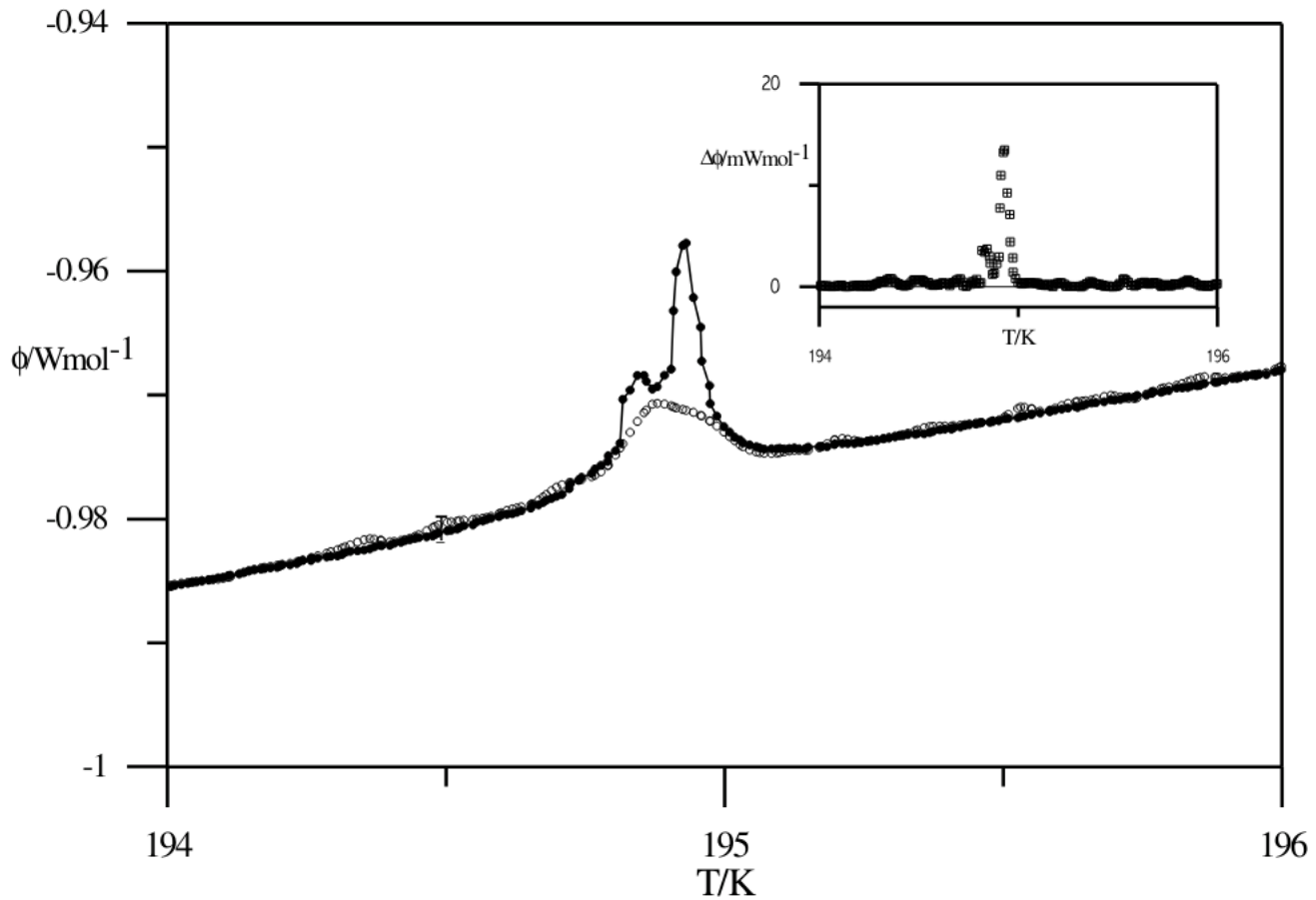


FIG. 2. This is the same as figure 1, but for the commensurate-incommensurate phase transition. Left axis: (full circle) are used for the measured heat flow while (open circle) are used for the deduced background contribution. Right axis shows the difference between them (open square). This difference cannot be ignored and is related to the transition latent heat. As can be observed, width of the ϕ anomaly is $1K$ and corresponds to measurements of specific heat. But the latent heat peak ($\Delta\phi$), representing phase coexistence, appears only in $0.2K$.

tent heat from transition enthalpy -which includes latent heat and the integral of specific heat in respect to temperature - in this type of compound has barred rigorous analysis of the specific heat anomaly for this transition. Before [7], specific heat in the domain-like zone was studied in cases where there was expectancy that domain walls would interact with a repulsion potential. Under these conditions the result obtained was that specific heat diverged in accordance with $(T - T_{ic})^{-1}$, as verified experimentally. Moreover, it became obvious that contribution to transition enthalpy by this specific heat was significant and that latent heat could not be regarded as being the same as transition enthalpy. Analyzing this divergence the conclusion was that latent heat should be, at most, $3 J mol^{-1}$.

From a theoretical point of view, in order to study commensurate-incommensurate phase transition discontinuity one must get away from the domain-like regime and introduce an attraction term into the system's thermodynamic potential. In doing so, and following the no-

tation of reference [7] the latent heat is obtained as:

$$Q = T_{loc} \frac{P_s^2}{C_2} \left(\ln \frac{a_2/a_1}{2(T_{ic} - T_{loc})} \right)^{-1}, \quad (3)$$

where P_s is spontaneous polarization in transition temperature, and C_2 is Curie's constant for permittivity, T_{ic} is the temperature where domain formation becomes favourable, T_{loc} is the temperature where phase transition actually occurs and a_1, a_2 are coefficients of the thermodynamic potential (to be considered constants). Thermodynamic theory for the incommensurate phase allows for relating logarithm in equation (3) with the wave vector in the incommensurate phase. This gives:[2, 7]

$$Q = \frac{2}{\pi} T_{loc} \frac{P_s^2}{C_2} \frac{q_{loc}}{q_0}, \quad (4)$$

where q_{loc} is the wave vector at the transition temperature and q_0 is value of the wave vector when forming in

the incommensurate phase.

For this sample, $4\pi C_2 = 68 \text{ K}$, whilst values of P_s and q_{loc} have been studied in a multitude of references. Their values are $0.11 \mu\text{C cm}^{-2}$ to $0.13 \mu\text{C cm}^{-2}$ for spontaneous polarization and between $\frac{1}{2}$ and $\frac{1}{6}$ for q_{loc}/q_0 [8–10]. With these data, the latent heat in the transition calculated in equation (4) has a value of 2 J mol^{-1} to 6 J mol^{-1} depending on whether $\frac{1}{6}$ or $\frac{1}{2}$ is used for q_{loc}/q_0 . Value obtained experimentally ($Q = 2.3 \text{ J mol}^{-1}$) agrees in order of magnitude with that calculated for expression 4 and seems to suggest that q_{loc}/q_0 is nearer $\frac{1}{6}$ than $\frac{1}{2}$.

An analysis can be made in order of magnitude relating thermal and dielectric properties of the commensurate-incommensurate transition. Specific heat diverges[7], in the zone of the domain-like regime, in the form of $(T - T_{ic})^{-1}$ and the ratio of proportionality of the law is:

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

which is similar to expression (3) except that temperatures appearing in the logarithm differ: T_1 being an intermediate temperature of the interval wherein the law of divergence of specific heat is in effect. However, we can assume that the order of magnitude of logarithms in equations (3) and (5) is similar, thus the order of magnitude is:

$$\frac{T_{ic} C_1 P_s^2}{C_2 Q^2} \sim 1. \quad (6)$$

Using the value [7], $C_1 = 0.158 \text{ J mol}^{-1}$, the member

on the left in equation (6) gives a value of 1.5 – 1.7. This result corroborates validity of the values for Q and C_1 . We wish to emphasize that in analysis of this expression all experimental data have been obtained from the same sample, except for that referring to spontaneous polarization.

Of further difficulty is the comparison of latent heat with the expression derived from the Clausius equation:

$$\frac{dT_{loc}}{dE} = -\frac{T_{loc} P_s}{Q}. \quad (7)$$

Value obtained from our data is:

$$\frac{dT_{loc}}{dE} \sim 1.3 \text{ K cm V}^{-1}, \quad (8)$$

whereas measurements in Fousek *et al.* [14] produce a value of 0.50 K cm V^{-1} . Nevertheless, these measurements were taken from a lower quality crystal than that used in the present experiment, which could account for the difference.

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