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Evidence of latent heat in the Rb₂ZnCl₄ commensurate–incommensurate phase transition

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Abstract. The commensurate–incommensurate phase transition of a Rb₂ZnCl₄ crystal was studied using a conduction calorimeter. By identifying the contribution of the specific heat to the transition enthalpy it was possible to show, for the first time for a compound of this type, transition latent heat. This was estimated to be $Q = 2.3$ J mol^{-1}. The result was compared with theoretical predictions for a domain wall model having repulsive–attractive interaction; satisfactory results were obtained for the first time. The same analysis was applied to the normal–incommensurate phase transition and no latent heat was observed, as expected.

1. 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 is maintained independently of the nature of the system [1–3]. To establish that this phase transition is present, the study must include the normal–incommensurate phase transition always present at higher temperature. When this is done, the mathematical framework of the commensurate–incommensurate phase transition becomes considerably more complicated as shown in references [2] and [4]. The purpose of this work is to analyse the latent heat in the commensurate–incommensurate phase transition in Rb₂ZnCl₄; hence a simpler analysis can serve us, 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 (see reference [5]); the force of interaction between domain walls is a determining factor when describing properties of the transition: if the interaction were purely repulsive, the transition would be continuous. However, there are always attraction forces in ferroelectric structural transitions that cause the transition to be discontinuous [6, 7]. Within this model the existence of a well-defined domain wall structure is assumed, although it is, experimentally, hardly realizable.

 Repulsion forces between domain walls are dominant over a wide range of temperatures above the transition temperature and yield theoretical expressions for the divergences of the dielectric susceptibility and specific heat, as in reference [2]. Experimentally, the anomaly of the dielectric constant was analysed within this formalism by Levstik *et al* [8], who

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ascertained that it diverged from the $(T - T_{ic})^{-1}$ law precisely as set forth theoretically. The specific heat peak was described as a manifestation of the transition's discontinuous nature, but recently [9] proof has been found 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 [10–12], or birefringence [13], display certain characteristics implying a discontinuous transition and indicate that, within a given temperature range approaching the transition temperature, the presence of attractive forces is not to be discounted. Within this temperature range, corresponding to the final part of the permittivity peak and specific heat, predictions within the repulsion model do not hold true [9].

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 the 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* [14] used the integral of the anomaly of the specific heat in the Clausius–Clapeyron formula, implicitly assuming that it meant latent heat. On the other, Zhu *et al* [15] estimated the latent heat of *barium sodium niobate* (BSN) from DSC measurements. In neither of the two instances were the two previously mentioned contributions taken into account.

Nonetheless, theoretical analysis of the phase transition shows that the 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 of proportionality (three–four orders of magnitude less than the permittivity in the same transition phase). Therefore, the specific heat anomaly is detectable only within a temperature range nearing T_{ic} (approximately 1 K). In contrast, estimations from the Clapeyron formula indicate latent heat of the order of a few joules per mole [16]. In consequence, it becomes necessary to analyse 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 mentioned. This technique was applied in establishing the latent heat for the commensurate–incommensurate transition in the Rb_2ZnCl_4 crystal. To cross check the method, the same procedure was used on the normal–incommensurate phase transition, which is a continuous transition where the enthalpy variation results solely from the specific heat.

2. Experimental procedure

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 mm^2 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 a^*. Finally, at $T_{ic} = 195$ K, the crystal phase locks into a commensurate phase which is again orthorhombic ($Pna2_1$) but is ferroelectric along the c-axis and with a triple unit cell [17]. Rb_2ZnCl_4 has been widely chosen as a test case for the theoretical description of both the commensurate–incommensurate phase transition and the normal–incommensurate phase transition.

The conduction calorimeter has been described elsewhere [18]. Briefly, it consists of a large calorimetric block whose mass makes it a thermal reservoir. Two fluxmeters together form a set of 96 thermocouples constructed thermally in parallel and electrically in series;

one junction from 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 the two heaters (allowing thermal excitation of the sample). Special care is taken in conserving the axial symmetry of the assembly. By making a 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 in 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 the equilibrium state [19].

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

Theoretically, well away from the transition point the heat flux should be proportional [20] to the rate of temperature change, and the heat capacity of the sample and its surroundings (fluxmeters, silver electrode and heaters). That is,

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

Here C_s is the sample heat capacity and C_0 represents the heat capacity of the surroundings. This value can be obtained by giving the sample heat capacity and calibrating C_0 as we will show in section 3. The existence of latent heat can be shown by measuring ϕ and comparing with ϕ_0. The latent heat will be obtained as

$$Q = \int (\phi - \phi_0)\, dt \tag{2}$$

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 Rb₂ZnCl₄ sample was set in the conduction calorimeter and cooled in the paraelectric phase to 100 K. Afterwards, the sample was heated at a constant rate of 2 K h^{-1} to room temperature whilst the fluxmeter thermoelectromotive force signals were registered as functions of temperature. The thermoelectromotive force was recorded by a *Keithley K182* nano-voltmeter. At 190 K and 200 K the calorimeter was calibrated [18] in order to convert the fluxmeter signal into heat flow. A similar experiment was performed near the normal–incommensurate phase transition.

3. 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 the sample mole number. The anomaly in the signal is due to variation of the 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 the heat flux and the sample heat capacity (the latter being measured for the same calorimeter and sample, and shown in the inset in figure 1) at two temperatures distant from the 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 dT/dt being known, we determine C_0 at these temperatures and then we are able to determine the
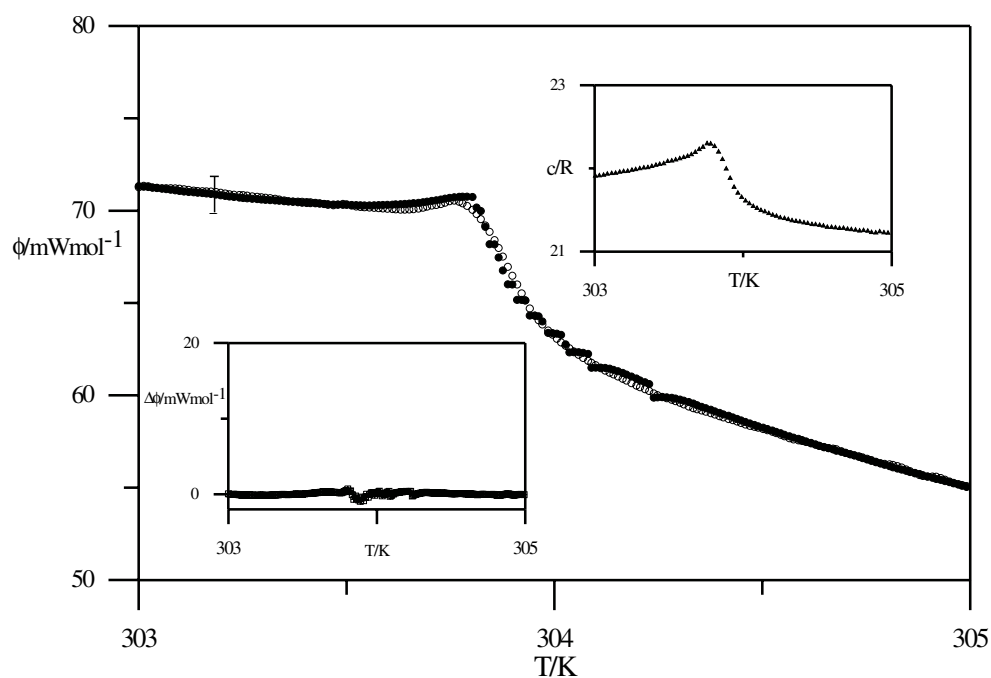
Figure 1. The measured heat flux (●) and the background contribution (○) deduced from specific heat data in the neighbourhood of the normal–incommensurate phase transition. The specific heat—see the upper-right inset—was measured in the same calorimeter on the same sample. The heat capacity contribution (see equation (1)) matches with the measured heat flux. The bottom-left inset shows the deviation of the heat flow from the background; the scale of the inset is that of figure 2. Data are randomly placed around the zero point. Thus, no latent heat is observed within experimental resolution in agreement with the 3d XY universality class of this phase transition. The error bar represents ± 1 mW mol^{-1}.

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 the specific heat measured in the transition, ϕ_0 can be calculated as a function of temperature by again invoking 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, the measured heat flow and what is expected due to excess specific heat are exact matches in form and value. The deviation ($\Delta\phi$) is shown in the bottom-left inset: their maximum is less than 1 mW mol^{-1} and it is randomly greater and less than zero. Therefore the only contribution to the transition enthalpy is excess specific heat, and the resulting latent heat is zero (within the equipment's resolution). This is the result to be expected for this transition which belongs in universality class 3d XY.

In figure 2 the same analysis is shown, but near the commensurate–incommensurate phase transition. The measured heat flow, ϕ, which includes contributions from the latent heat and specific heat, is represented by full circles. The heat flow ϕ_0, calculated from specific heat data, is represented by open circles. In the upper-right inset we show the $\Delta\phi$ data. In the present case, the maximum deviation is 13 mW mol^{-1} and a peak is seen at the commensurate–incommensurate phase transition. Thus, our data show that the enthalpy variation cannot be explained solely by means of the specific heat contribution and, therefore, show the presence of latent heat. The integral of equation (2) is evaluated for $Q = 2.3$ J mol^{-1}. The transition
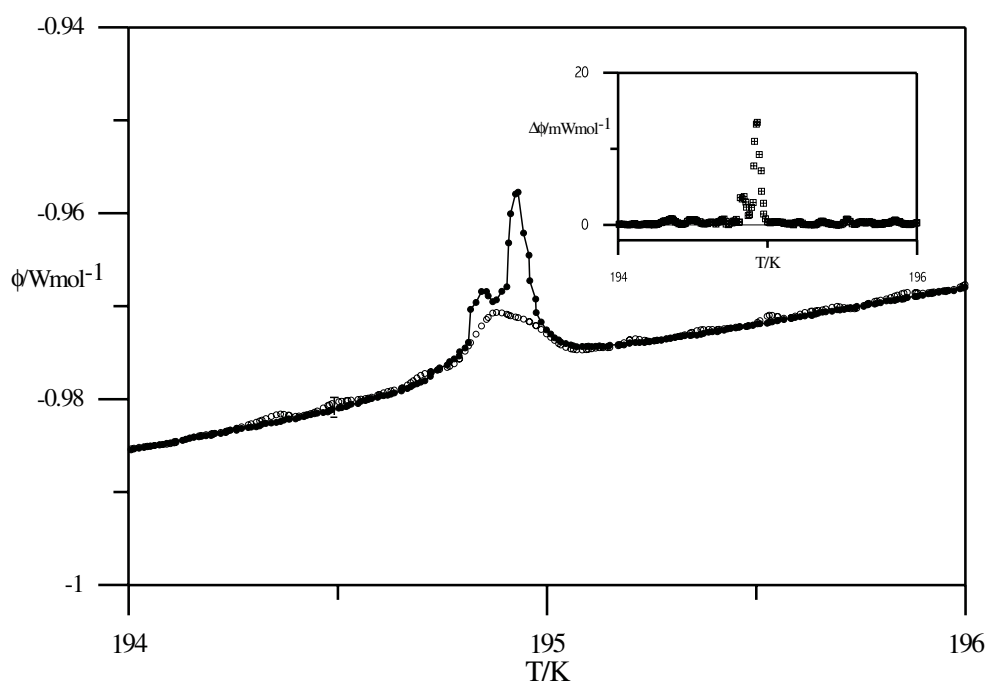
Figure 2. As figure 1, but for the commensurate–incommensurate phase transition. The ● stand for the measured heat flow while the ○ are used for the deduced background contribution. The specific heat is that of reference [9]. The error bar represents ±1 mW mol^{-1}. The inset shows their differences. The latent heat peak ($\Delta\phi$), representing phase coexistence, is only 0.2 K wide. The $\Delta\phi$ maximum is 13 mW mol^{-1} and the peak area is 2.3 J mol^{-1}.

entropy is then $1.4 \times 10^{-3} R$ which is much less than the order–disorder entropy $R \log(2)$. Also significant is the apparent double peak, which cannot be interpreted in terms of the specific heat anomaly: to our knowledge there is no other evidence of such a phenomenon in specific heat measurements for the commensurate–incommensurate phase of Rb$_2$ZnCl4. A comprehensive study of this shoulder lies outside of the scope of this paper; it could be due to some kinetic process in the transition, a microscopic feature of the transition or a new extremely unstable incommensurate phase.

4. Discussion

The greatest difficulty in identifying the 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 $dT/dt = 2$ K h^{-1}, the 0.2 K span means a six-minute interval, which is of the order of magnitude of the relaxation of the calorimeter. While we have explained the peak's width, the shape of the anomaly, with its double peak, is quite different from that expected of a specific heat anomaly, so this area represents a close approximation of the 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 latent heat from transition enthalpy—which includes latent heat and the integral of the specific heat with respect to temperature—for this type of compound has barred rigorous analysis of the specific heat anomaly for this transition. Previously [9], specific heat in the domain-like zone was studied in cases where there was an expectation that domain walls would interact with a repulsion potential. Under these conditions the result obtained was that the specific heat diverged in accordance with $(T - T_{ic})^{-1}$, as verified experimentally. Moreover, it became obvious that the contribution to the transition enthalpy made by this specific heat was significant and that latent heat could not be regarded as being the same as transition enthalpy. Analysing this divergence, the conclusion was that the latent heat should be, at most, 3 J mol^{-1}.

From a theoretical point of view, in order to study the 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. On doing this, and following the notation of reference [9], the latent heat is obtained as

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

where P_s is spontaneous polarization at the transition temperature, C_2 is Curie's constant for permittivity, T_{ic} is the temperature at which domain formation becomes favourable, T_{loc} is the temperature at which the 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 the relating of the logarithm in equation (3) with the wave vector in the incommensurate phase. This gives [2, 9]

$$Q = \frac{2}{\pi} T_{loc} \frac{P_s^2}{C_2} \frac{q_{loc}}{q_0} \tag{4}$$

where q_{loc} is the wave vector at the transition temperature and q_0 is the value of the wave vector during the formation of the incommensurate phase.

For this sample, $4\pi C_2 = 68$ K, whilst the values of P_s and q_{loc} have been studied in a multitude of references. Their values are 0.11–0.13 μC cm^{-2} for spontaneous polarization and between $\frac{1}{2}$ and $\frac{1}{6}$ for q_{loc}/q_0 [10–12]. With these data, the latent heat in the transition calculated in equation (4) has a value of 2–6 J mol^{-1} depending on whether $\frac{1}{6}$ or $\frac{1}{2}$ is used for q_{loc}/q_0. The value obtained experimentally ($Q = 2.3$ 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 order-of-magnitude analysis can be made relating the thermal and dielectric properties of the commensurate–incommensurate transition. The specific heat diverges [9], 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

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

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

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

Using the value [9] $C_1 = 0.158$ J mol^{-1}, the expression on the left in equation (6) gives a value of 1.5–1.7. This result corroborates the validity of the values for Q and C_1. We wish

to emphasize that in the analysis of this expression all of the experimental data have been obtained for the same sample, except for those relating to the spontaneous polarization.

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

$$\frac{\mathrm{d}T_{loc}}{\mathrm{d}E} = -\frac{T_{loc}P_s}{Q}.$$ (7)

The value obtained from our data is

$$\frac{\mathrm{d}T_{loc}}{\mathrm{d}E} \sim 1.3 \text{ K cm V}^{-1}$$ (8)

whereas the measurements by Fousek and Kroupa [16] produce a value of 0.50 K cm kV^{-1}. Nevertheless, these measurements were made on a crystal of lower quality than that used in the present experiment, which could account for the difference.

5. Conclusions

The question of whether commensurate–incommensurate phase transitions are discontinuous or continuous has impeded a lot of discussion both theoretically and experimentally. Although it has been widely stated that, experimentally, they are found to be discontinuous, and some theoretical papers have also supported this point of view (see for instance references [6] and [7]), there has been no experimental evidence found of latent heat in the phase transitions. Our experiments have been carried out on the same sample, and by comparing the normal–incommensurate phase transition and the commensurate–incommensurate phase transition in Rb$_2$ZnCl$_4$ we can conclude that latent heat exists and give a reasonable value, for the first time. As previously expected [9], the transition entropy is much less than the order–disorder limit. This low value explains why it is difficult to observe. Anyway, the value agrees in order of magnitude with a phenomenological theory which takes into account domain wall interactions.

On the other hand, our data show a new feature of the phase transition: the shoulder shown in figure 2. The study of macroscopic quantities such as thermal properties reveals to us its origin. However, previously reported data on specific heat [9, 14, 21] have not revealed a kink or shoulder at this point. New microscopic experiments will be welcome, but these lie, at present, beyond our capabilities.

Acknowledgments

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