Specific heat of a β-$Tb_2(MoO_4)_3$ crystal in the region of the nonideal ferroelectric phase transition

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(Submitted 19 January 1995)
Zh. Éksp. Teor. Fiz. **108**, 373–380 (July 1995)

The specific heat of the nonideal ferroelectric terbium molybdate has been measured over the broad temperature range from 85 K to 560 K. Two anomalies, one at the ferroelectric phase transition at $T_0 = 429.79$ K and the other in the vicinity of 271 K, have been discovered. The temperature dependence of the lattice specific heat has been approximated using a Debye function and three Einstein functions, the anomalous part has been isolated, and the critical indices have been determined near T_0 under the assumption of a first-order phase transition near the critical point.

1. INTRODUCTION

The rate-earth molybdates $R_2(MoO_4)_3$ (R=Gd, Eu, Dy, Sm, Tb) are known to be nonideal ferroelectrics, in which the phase transition is accompanied by doubling of the unit cell in the ferroelectric phase and condensation of a lattice vibrational mode at the $M(110)(\pi/a)$ point of the Brillouin zone.[1,2] A description of such phase transitions based on the Landau theory was proposed by Levanyuk and Sannikov[3,4] and made it possible to explain the unusual temperature dependence of the spontaneous polarization, the elastic properties, and the dielectric susceptibility of the crystals, which differ significantly from the case of ideal ferroelectricity.

Although the properties of gadolinium terbium molybdates were thoroughly investigated in the seventies, mainly in connection with the problem of the correspondence of the phenomenological theory to the experimental data,[5] no special attention was focused on the role of fluctuation effects in nonideal ferroelectric phase transitions. This was possibly due to the fact that the phase transitions in rare-earth molybdates were found to be first-order and to occur close to the triple point. According to Ref. 2, in the paraelectric phase of terbium molybdate, linear extrapolation of the temperature dependence of the square of the frequency of the soft mode to zero value gives $T_c = 149$ °C, while the first-order phase transition takes place at $T_0 = 160$ °C. At the same time, deviations from the "regular" (Landau) dependences of the elastic moduli and the dielectric constant of gadolinium molybdate were observed at $T > T_0$, pointing to a possible significant role for fluctuation effects in nonideal ferroelectric transitions.

It was not ruled out that the abrupt character of the phase transitions in nonideal ferroelectrics, i.e., rare-earth molybdates, is caused specifically by fluctuation renormalization of the Landau expansion coefficients.[8,9] It was recently shown that such a possibility is realized in the form of a jump in the order parameter at $T = T_0$, which is comparable to its value far from T_0, at least for displacive structural phase transitions described by a one-component order parameter.[10] In nonideal ferroelectrics the phase transition is described by a two-component order parameter, and spontaneous polarization appears as a secondary effect.

It would be useful to reinvestigate the phase transition in crystals of $Tb_2(MoO_4)_3$ (TMO) from the standpoint of elucidating the role of the critical fluctuations of the order parameter by performing precision measurements of the specific heat in the vicinity of the phase transition, especially since the published data regarding the thermal properties of crystals of rare-earth molybdates are open to various interpretations. The available publications on the temperature dependence of the specific heat of gadolinium molybdate[11,12] state that there is logarithmic divergence of the specific heat in a broad temperature range below T_0. The measurements performed by the dynamic method on terbium molybdate crystals also revealed significant disparity between the data obtained and evaluations based on the Landau theory.[13] When the experimental data were analyzed in Refs. 11–13, proper attention was not focused on isolating the contribution of the lattice specific heat, whose temperature dependence was assumed to be linear in the region of the phase transition.

This paper presents the results of an investigation of the caloric properties of the nonideal ferroelectric $Tb_2(MoO_4)_3$ over a broad temperature range and near the phase transition point using ac and adiabatic calorimetry.

Since the relatively high temperature of the phase transition $T_0 = 429.79$ K makes it difficult to investigate critical phenomena with adiabatic calorimetry, we used this method only for measurements in the 100–365 K temperature range; the data obtained were used to convert the relative values of

1063-7761/95/070202-05$10.00

TABLE I.

T, K	C_p, J/kg·K
103.2	255.4
122.8	297.3
140.0	326.6
160.1	351.7
183.0	368.4
201.2	397.7
223.0	410.3
245.0	422.9
273.1	448.0
301.8	468.9
324.4	489.9
342.7	498.2
363.0	515.0

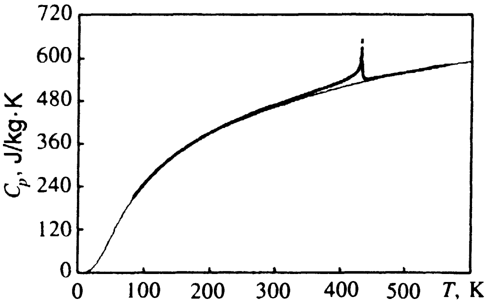

FIG. 1. Temperature dependence of the specific heat of a TMO crystal in the 85–560 K temperature range. The lattice specific heat determined in accordance with Eq. (1) is represented by the thin line.

the specific heat obtained by ac calorimetry in the 85–560 K temperature range to absolute values. The measurements were performed using a Sinku-Riko model ACC-1 M/L ac calorimeter at a frequency of 1 Hz. Utilizing the high temperature resolution and sensitivity of this calorimeter, we obtained a sufficient number of points near the phase transition for analysis.

The TMO single crystal was grown by the Czochralski method in an apparatus with inductive heating, which was equipped with a system for automatically monitoring the weight of the growing crystal. The crystal was grown in air from a platinum crucible in the [001] direction at a withdrawal rate equal to 3–8 mm/h and a rotation rate equal to 100 rpm. Samples were cut from the single-crystal boule by a diamond saw. The dimensions of the samples were of the order of 1 cm^3 in the case of measurements on the adiabatic calorimeter and $3\times3\times0.1$ mm^3 in the case of the measurements on the ac calorimeter.

The treatment of the experimental data obtained involved "matching" the data obtained by the absolute and dynamic methods, constructing the temperature dependence of the lattice (phonon) specific heat, isolating the excess specific heat, analyzing its analytical form, and determining the excess energy and entropy associated with the nonideal ferroelectric phase transition in the terbium molybdate crystals.

Table I presents the absolute values of the specific heat of a $Tb_2(MoO_4)_3$ crystal obtained by adiabatic calorimetry in the 100–365 K range, and Fig. 1 presents the temperature dependence of the specific heat determined by the dynamic ac method in the 85–560 K temperature range with the scale on the vertical axis obtained by comparing the experimental values with the data from Table I. The error in the determination of the scale caused by the inaccuracy of the adiabatic method amounts to 0.4%. The curve in Fig. 1 represents a total of more than 3500 experimental points. The thin line shows the temperature dependence of the phonon specific heat determined by "matching" with experimental points below 200 K and above 500 K using an equation of the form

$$C_p^{\mathrm{lat}}=C_1\mathscr{D}(\Theta_D/T)+C_2\mathscr{E}(\Theta_{E1}/T)+C_3\mathscr{E}(\Theta_{E2}/T)+C_4\mathscr{E}(\Theta_{E3}/T)+C_5T, \tag{1}$$

where $\mathscr{D}$ and $\mathscr{E}$ are Debye and Einstein functions, and Θ_D, Θ_{Ei}, are C_i are fitting parameters. The "Debye temperature" Θ_D was selected on the basis of the values of the specific heat in the vicinity of 100 K. The best agreement with the deviation of the phonon specific heat from the experimental points (no more than 0.4% on the 85–120 K and 485–560 K segments of the curve) was obtained with the following values of the fitting parameters:

$$\Theta_D=294\ \mathrm{K},\quad \Theta_{E1}=625\ \mathrm{K},\quad \Theta_{E2}=757\ \mathrm{K},$$

$$\Theta_{E3}=1650\ \mathrm{K},$$

$$C_1=348.80\ \mathrm{J/kg\cdot K},\quad C_2=131.62\ \mathrm{J/kg\cdot K},$$

$$C_3=13.162\ \mathrm{J/kg\cdot K},$$

$$C_4=180.981\ \mathrm{J/kg\cdot K},\quad C_5=0.029680\ \mathrm{J/kg\cdot K^2}.$$

The anomalous part of the specific heat is presented in Fig. 2. It is seen that apart from the principal anomaly in the vicinity of the temperature of the nonideal ferroelectric phase transition $T_0=429.79$ K, the plot of the temperature dependence of the excess specific heat exhibits an additional anomaly in the form of a smeared maximum located in the 250–300 K temperature range.

The excess entropy and energy associated with the anomalous part of the specific heat were determined by integration:

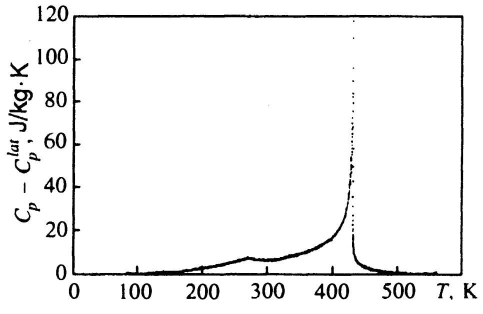

FIG. 2. Temperature dependence of the excess specific heat of a TMO crystal.

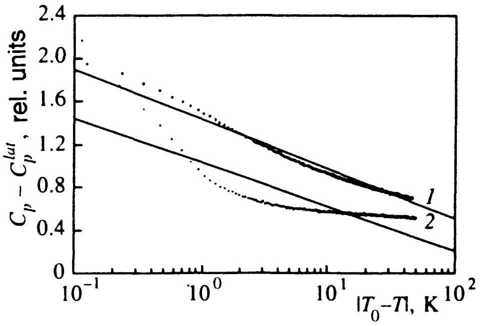

FIG. 3. Temperature dependence of the excess specific heat of a TMO crystal plotted on a logarithmic scale. The straight lines were drawn through the corresponding points by the least-squares method: *1)* $T<T_0$; *2)* $T>T_0$.

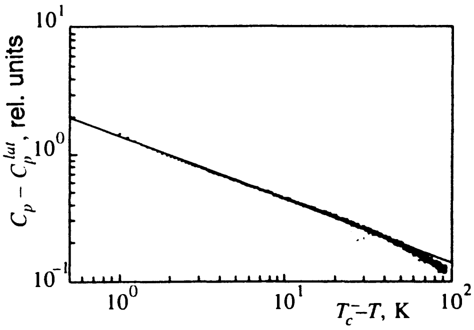

FIG. 4. Temperature dependence of the excess specific heat of the low-temperature phase of a TMO crystal plotted in log–log coordinates. The straight line corresponding to $\alpha' = 0.5$ was drawn by the least-squares method through the experimental points corresponding to the temperatures $(T_c^- - T) < 48$ K. $T_c^- = 430.67$ K.

$$\Delta Q = \int_{120\,\mathrm{K}}^{485\,\mathrm{K}} (C_P - C_P^{\mathrm{lat}})dT = 2680 \pm 20 \ \mathrm{J/kg},$$

$$\Delta S = \int_{120\,\mathrm{K}}^{485\,\mathrm{K}} \frac{C_P - C_P^{\mathrm{lat}}}{T} dT = 7.96 \pm 0.04 \ \mathrm{J/kg \cdot K},$$

We note that the true values of both parameters may be somewhat greater, since the latent heat of the phase transition is not detected by ac calorimetry.

The analytic form of the temperature dependence of the excess specific heat was ascertained by comparing the experimental points with logarithmic and power functions. The analysis is very difficult in the present case, since the difference between the temperature of the specific heat maximum T_0 and the temperatures T_c^+ and T_c^-, which specify the asymptotes of the corresponding temperature dependences in the symmetric and asymmetric phases upon the first-order phase transition must be taken into account. The treatment of the experimental data in accordance with the relation

$$C_P - C_P^{\mathrm{lat}} = A \ln \left| 1 - \frac{T}{T_0} \right|, \tag{2}$$

$(T_0 = T_c^+ = T_c^-)$ after Ref. 12 (see Fig. 3) did not provide evidence in support of a logarithmic dependence: the "dip" along the experimental curves and the nonlinear character of the plots were obvious in both phases.

A further analysis was carried out in the context of a possible power-function dependence of the excess specific heat on the temperature according to the relation

$$C_P - C_P^{\mathrm{lat}} = A_{+,-} \left| 1 - \frac{T}{T_c^{+,-}} \right|^{-\alpha,\alpha'}, \tag{3}$$

where A_-, T_c^-, and α' correspond to the low-symmetry phase, and A_+, T_c^+, and α correspond to the high-symmetry phase.

The values of T_c^- and T_c^+ were selected so as to achieve agreement between this dependence and the experimental data over as broad a temperature range as possible. A value close to $T_0 - 10$ K is most probable for T_c^+, in accordance with Ref. 2. Here we assumed that the points in the immediate vicinity of T_0 are less reliable due to the defect-induced "broadening" of the δ function caused by the latent heat of the first-order phase transition.

It is seen in Fig. 4 that below the temperature of the phase transition, the experimental points are described well by relation (3) with the values $\alpha' = 0.50 \pm 0.03$, $T_c^- = 430.67$ K, and $A_- = 4.5 \pm 0.4$ J/kg·K. This value of the critical index is also supported by the results of a treatment of the experimental data using the following relation, which follows from the Landau theory and holds for first- and second-order phase transitions near the critical point:

$$\left(\frac{C_P - C_P^{\mathrm{lat}}}{T} \right)^{-2} = \left(\frac{C_P - C_P^{\mathrm{lat}}}{T} \right)^{-2}_{T=T_0} + K(T_0 - T), \tag{4}$$

where K is a constant, which is a function of the coefficients in the expansion of the thermodynamic potential in invariant combinations of the components of the order parameter. Figure 5 presents experimental points and a straight line corresponding to Eq. (4). It is seen that Eq. (4) accurately describes the temperature dependence of the specific heat in the ferroelectric phase over a broad temperature range, and the deviation from the straight line at $T_0 - T < 3$ K is attributable to the overestimated values of $C_P - C_P^{\mathrm{lat}}$ due to the contribution of the latent heat of the transition, which is "smeared"

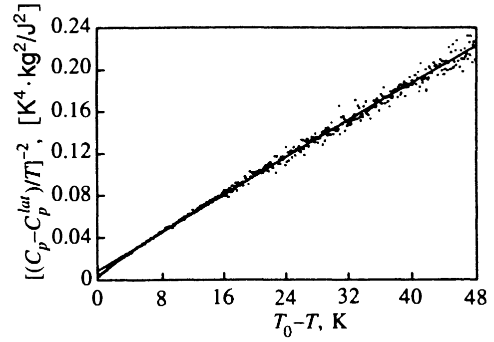

FIG. 5. Excess specific heat of the low-temperature phase of a TMO crystal represented in the form of Eq. (4). The straight line was drawn through the points presented by the least-squares method.

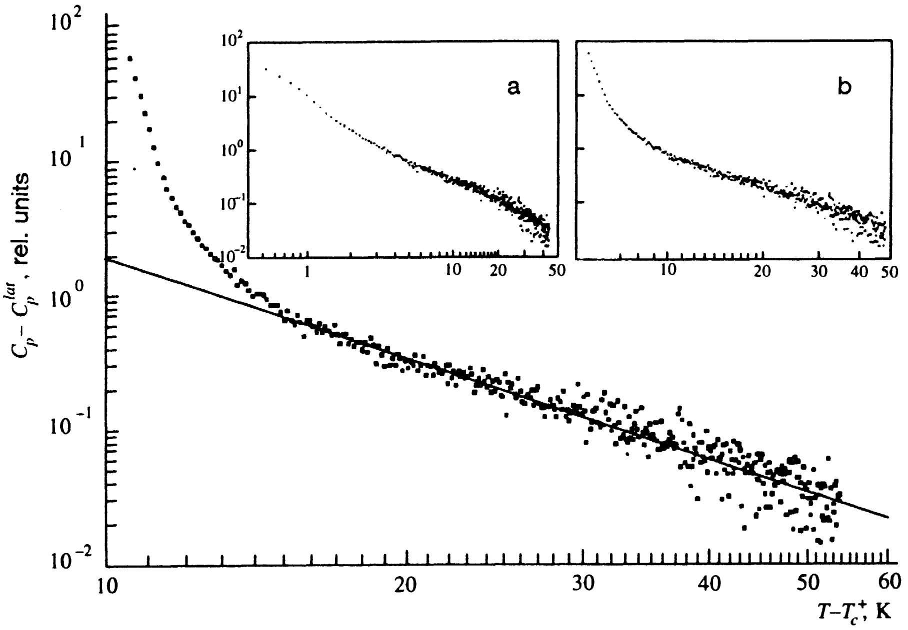

FIG. 6. Excess specific heat of the high-temperature phase of a TMO crystal in log–log coordinates. The straight line corresponds to $\alpha = 1.35$ and $T_c^+ = 419.5$. Insert a) $T_c^+ = 429.5$ K. Insert b) $T_c^+ = 424.5$ K.

by the crystal defects and the inaccurate selection of the value of T_c^-. The value of T_c^- was determined under the assumption that there is a single critical index for the low-symmetry phase. Straight lines were drawn through the experimental points for different values of T_c^- by the least-squares method, and the magnitude of their deviations was determined. The smallest deviations corresponded to $T_c^- = 430.5 \pm 0.2$ K and to a critical index $\alpha' = 0.50 \pm 0.03$. When T_c^- was increased from that value, the effective value of the critical index increased.

As noted above, a considerable portion of the excess energy of the phase transition belongs to the temperature range $T > T_0$: the anomalous part of the specific heat is detected up to 475 K, i.e., 35–40 K above the point of the phase transition. It is interesting that an appreciable portion of the excess energy and entropy was obtained at $T > T_0$ ($\Delta Q_{T > T_0} = 230 \pm 15$ J/kg, $\Delta S_{T > T_0} = 0.50 \pm 0.02$ J/kg·K).

Let us discuss the possible analytic form of the temperature dependence of the excess specific heat at $T > T_0$.

It is seen from Fig. 6 that a description of the entire temperature range using a single critical index can be achieved by varying the value of T_c^+ as T_c^+ decreases, the values of the specific heat correspond more and more closely to Eq. (3); when $T_c^+ = 419.5 \pm 0.3$ K (i.e., a temperature which corresponds approximately to the vanishing of the frequency of the soft mode extrapolated according to Ref. 2), the experimental points plotted in log–log coordinates are concentrated around the straight line corresponding to a value of the critical index $\alpha = 1.35 \pm 0.15$.

It is clear that the value of the critical index α obtained for the symmetric phase is too high to be associated with the critical phenomena caused by fluctuations of the order parameter.[14] On the other hand, $\alpha \approx 3/2$ was obtained in several investigations under the assumption that the local distortions of the crystal structure caused by various types of defects contribute to the anomalous static properties.[15,16] It is remarkable that an investigation of the temperature dependence of the low-frequency elastic compliance s_{11} in the region of the structural phase transition in $SrTiO_3$ crystals yielded a value of the critical index $\mu = 1.5 \pm 0.2$ ($T > T_c$) and that a calculation of the contribution of a system of noninteracting defects in the model of a Heisenberg fixed point gave $\mu = 1.3$, which is close to the experimental value.[17] It was shown in Ref. 18 that in nonideal ferroelectrics containing the invariant $\eta_i \eta_j E_k$ in the thermodynamic potential (η_i is a component of the order parameter, and E_k is a component of the electric field vector), which include, in particular, rare-earth molybdates, the formation of "frozen" regions with the symmetry of the low-temperature phase can be expected at $T > T_c$ near defects which have an intrinsic electric charge. As the calculation in Ref. 18 shows, in this case the contribution of the defects to the specific heat increases proportionally to $(T - T_c)^{-3/2}$ as the phase transition point is approached. It is possible that just this case is realized in our experiment.

Let us discuss the presence of an additional broad maximum in the temperature dependence of the excess specific heat, which was revealed only after careful subtraction of the lattice specific heat and was not previously noted in the literature. The form of the anomaly, which is unusual for first- and second-order structural phase transitions and which was clearly reproduced in repeated measurements, does not make it possible to unequivocally state that a new phase transition occurs in the TMO crystal. On the other hand, the similarity between the temperature dependence of the specific heat obtained in the 250–300 K range and the corresponding dependence for a crystal of $(CH_3NH_3)_5Bi_2Cl_{11}$ recently obtained in Refs. 19 and 20 is noteworthy; in the latter case the anomaly was unequivocally associated with "traces" of a critical point on a line of isostructural first-order phase transitions: the supercritical character of the change in the phase state in these crystals was established in Ref. 21. Thus, we can now only postulate that there is a line of isostructural first-order phase transitions ending at the final critical point on the $P-T$ phase diagram of TMO crystals and that the "thermodynamic path" realized at normal pressure corresponds to bypassing the final point on the side of the supercritical states. We note that the possibility of the appearance of lines of isostructural phase transitions in the phase diagrams of rare-earth molybdates was noted in Ref. 19 on the basis of a description of the phase transitions in them from the standpoint of the theory of singularities.

In conclusion, we summarize the main results obtained in the present work.

1. The specific heat of a TMO crystal has been measured over a broad range of temperatures and near the point of the nonideal ferroelectric phase transition using different methods of precision calorimetry.

2. A quantitative analysis of the analytic form of the critical anomaly of the excess specific heat has been performed, and the nearly tricritical character of the phase transition at $T=T_0$ with $\alpha'\approx 0.5$ and $\alpha\approx 1.35$ has been confirmed. Thus, the earlier data on the logarithmic divergence of the specific heat in this crystal has not been confirmed.

3. The presence of an additional specific heat anomaly, which attests to the possible existence of a new line of isostructural phase transitions on the phase diagram of TMO crystals, has been established.

This research was performed with support from the Russian Fund for Fundamental Research (Projects Nos. 93-02-14712 and 92-02-03661) and the International Science Foundation (Grant No. M05300).

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Translated by P. Shelnitz