

On the thermodynamics of face-centered tetragonal \rightleftharpoons face-centered cubic transitions in indium alloys

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Anomalies in the specific heat in fct \rightleftharpoons fcc transformations in In - Cd and In - Tl alloys are studied experimentally and the temperature shifts of the transitions due to hydrostatic pressure are determined. Estimates of the integral volume and heat effects of the transitions are obtained. Some features of the thermodynamics and kinetics of the transformations due to the presence of shear and dilation and to the formation of domains and internal stress fields are discussed. On the basis of an analysis of the results of the present paper and from the literature it is concluded that the cubic phase of pure indium should be thermodynamically stable at negative pressures.

Pure indium in the solid state has a face-centered tetragonal structure with an axis ratio $c/a \sim 1.08$ at room temperature^[1]. With increasing temperature, the ratio c/a decreases^[1,2], but the indium lattice remains tetragonal up to the melting point. The ratio c/a also decreases when elements with lower valence-electron concentrations (He, Cd) are dissolved in it^[3,4], and also upon dissolution of Tl, which is isoelectronic with In^[5]. The fct \rightarrow fcc transition in indium alloys above room temperature corresponds to Cd contents of 4-5 at.%^[4] or Tl contents 18-21 at.%^[5]. The degree of tetragonality drops abruptly to unity from a value ~ 1.02 in In-Tl alloys^[5] and from a value ~ 1.04 in In-Cd alloys^[4]. The alloys In-Tl and In-Cd are convenient model systems for the study of phase transitions accompanied by weak distortions of symmetrical crystalline structures^[6]. Similar distortions accompany the processes of atomic ordering (CuAu, CuPt), magnetic (CoO) and ferroelectric (SrTiO₃) transformations, and also structure transitions in a number of superconducting compounds (V₃Si, Nb₃Sn, V₂Hf). These transitions are usually accompanied by very weak thermal and volume effects, the magnitudes of which have not been measured accurately in most cases.

For the thermal effects in In-Cd and In-Tl alloys there are only approximate estimates based on differential thermal analysis data^[7], and also on data obtained by the study of uniaxial tension and compression of the alloys in the fcc \rightleftharpoons fcc transition, reduced by using a modified Clapeyron-Clausius equation^[8]. In both cases, estimates yield values for the heats of transition on the order of $\sim 10^{-3}$ cal/g. Adiabatic-calorimeter measurements^[9] of the specific heat of polycrystalline alloys of In with 28.9% Tl undergoing an fcc \rightleftharpoons fcc transition at temperatures 70-100 K did not detect any latent heat of the transition. The only observed quantities were reproducible wave-like deviations from the smoothed values of the specific heat, exceeding 0.2%. The authors were unable to establish a correlation between the results of the measurements of C_p and the abrupt anomalies of the coefficient of thermal expansion $\alpha_{\langle 110 \rangle}$, which was previously established for this alloy in the phase-transition region^[10].

In model calculations of the mutual orientation, and also of the stability of the tetragonal and cubic phases in indium alloys^[11,12], the volume changes are usually neglected. According to the data of^[4,5], these changes

lie within the limits of the experimental errors of the dilatometric and x-ray methods. As a result of pycnometric investigations of the density^[7], it was concluded that the volume of an In-Cd or In-Tl alloy is reduced by $\sim 0.01-0.03\%$ (in an fct \rightleftharpoons fcc transition).

The purpose of the present work was experimental determination of the shift of the temperature of the fct \rightleftharpoons fcc transition in indium alloys under the influence of hydrostatic pressure (there are no published data on the subject), and direct measurement of the thermal effect of this transition using a precision microcalorimetric method.

PROCEDURE AND MEASUREMENT RESULTS

The principal measurements were made on alloys of In with 4.85 at.% Cd or 20.0 at.% Tl. The samples were prepared by fusing elements of 99.99% purity in evacuated glass ampules. The alloys were thoroughly stirred in the liquid state and then, to maintain homogeneous composition, were quenched from the melt in water. Since no loss of weight was observed, and the transition temperatures agreed with the published data, no subsequent chemical analysis of the samples was performed.

The influence of uniform hydrostatic pressure on the fct \rightleftharpoons fcc phase transitions was investigated by measuring the electric resistivity of samples of 0.2 mm diameter, prepared by extrusion of the alloys through a die at 20°C. The resistivity of the In-Tl alloys was measured immediately after the preparation of the wire samples, while that of the In-Cd alloys was measured a year after the extrusion. The sample was heated with a nichrome heater built into the high-pressure chamber. The temperature of the sample in the pressure chamber was measured with a chromel-alumel thermocouple with accuracy $\pm 1^\circ\text{C}$, while the pressure was measured with a calibrated manganin manometer with accuracy ± 200 bar. The pressure-transmitting medium was silicone fluid No. 5, which does not solidify up to 20 kbar.

The fct \rightleftharpoons fcc transition of the In + 4.85 at.% Cd alloy took place after heating to $\sim 79^\circ\text{C}$ and was accompanied by an increase of $\sim 0.5\%$ in the resistivity. The reverse transition was observed at $\sim 71^\circ\text{C}$. The transition temperatures in the course of heating and cooling were arbitrarily assumed to be the points corresponding to the maximal anomalies of the resistance. Figure 1 shows isobaric plots of the temperature dependence of

the resistivity of the alloy In + 4.85 at.% Cd at different hydrostatic pressures up to 5150 bar, taken with increasing temperature. The curves corresponding to cooling are similar in form. The complete heating-cooling cycle was performed in 20 minutes. Figure 2 shows the pressure dependences of the temperatures of the direct and reverse transitions of this alloy. The temperature hysteresis of the transition is practically independent of the pressure. The fct \rightleftharpoons fcc phase-equilibrium temperature increases linearly with increasing pressure, with a slope $dT/dP = (7.0 \pm 0.7)$ deg/kbar. At pressures above 5 kbar, the jumps on the temperature dependences of the resistivity begin to be smeared out, apparently as a result of the decreased solubility of the cadmium in the solid indium with increasing pressure, and as a result of the transition of the investigated alloy into the two-phase region. Similar data were also obtained for an alloy of indium with 4.6 at.% Cd, but in this case the temperatures of the fct \rightarrow fcc and fcc \rightarrow fct transitions at atmospheric pressure were respectively 90 and 81°C.

Investigations of the In + 20.0 at.% Tl alloy have shown that the anomaly of the resistivity at the fct \rightleftharpoons fcc phase transition point of this alloy is even smaller than for the In-Cd alloys. It has been established that, with the transition point fixed accurate to $\pm 2^\circ$, hydrostatic pressure up to 15 kbar does not shift the fct \rightleftharpoons fcc equilibrium temperature ($dT/dP = 0 \pm 0.5$ deg/kbar). Calorimetric measurements by the procedure described in^[13] were performed with an automatic-recording differential two-channel microcalorimeter^[14] adapted for operation in a heating and cooling cycle. The sensitivity of the calorimeter was 2×10^{-7} W. The calorimeter consisted of four pairwise connected cells, the time constants of which were ~ 30 sec and differed by not more than 5%. The heat exchange between the cells and the massive thermal screen of the calorimeter was registered with the aid of differential thermopiles made up of ~ 2000 chromel-copel thermocouples. The rate of change of the temperatures of the cells was monitored against a copper-constantan thermocouple placed in one of the free cells. To monitor the suitability of the method, we used the melting heat of small batches (~ 10 mg) of pure indium ($T_{\text{melt}} = 429.3^\circ\text{K}$) and mercury ($T_{\text{melt}} = 234.3^\circ\text{K}$). Comparison with the tabulated data^[15] has shown that the total error in the determination of the thermal effects in the calorimeter did not exceed $\pm 2\%$. In the investigation of the In-Cd and In-Tl alloys, the rate of change of the calorimeter temperature was 10 deg/hr, so that thermal effects down to 10^{-4} cal could be measured. The cali-

metric measurements were performed: a) on wire samples of In + 4.85 at.% Cd aged for a year, b) on freshly extruded wire samples of In + 4.85 at.% Cd and In + 20.0 at.% Tl, c) on cast bulky samples of both alloys. The bulky samples of the In-Cd alloy were also aged at room temperature for a year, while the bulky In-Tl samples were melted prior to the experiments and annealed at 130°C for 30 hours. The samples placed in the calorimeter weighed ~ 2 g.

Typical plots of the anomalous components of the specific heat ΔC_p in the transition regions, recorded with an automatic microcalorimeter and converted to the values per gram of alloy, are shown in Figs. 3 and 4.

The values of ΔC_p were reckoned from the regular temperature-dependence curves of the specific heats of the alloys, obtained by extrapolating the results of the measurements before and after the transitions. In the figures we have arbitrarily used negative and positive signs for the values of ΔC_p corresponding to endothermal and exothermal effects, respectively.

It is seen from Figs. 3 and 4 that the fct \rightleftharpoons fcc transitions proceed in both alloys with a noticeable temperature hysteresis (from 10 to 30°). The temperature region and the character of the transitions depend strongly on the shape, method of preparation, and thermal history of the sample. The temperatures of the direct and reverse transitions in a sample of aged In-Cd wire (Figs. 3b), which was taken from the same reel as the wire for the investigation of the resistivity at high pressure, are in good agreement with the transition temperatures obtained from resistometric measurements. The heat release accompanying the fcc

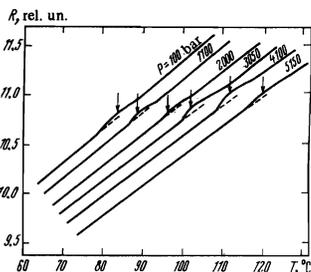


FIG. 1.

FIG. 1. Change of resistivity of In + 4.85 at.% Cd alloy (aged wire sample) in the course of heating under conditions of hydrostatic pressure.

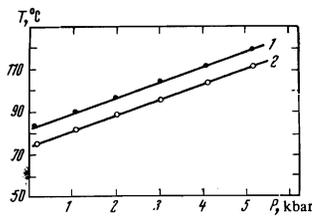


FIG. 2.

FIG. 2. Effect of pressure on the fct \rightarrow fcc (1) and fcc \rightarrow fct (2) transition temperatures in alloy In + 4.85 at.% Cd.

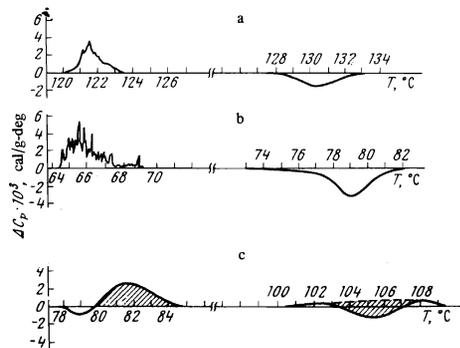


FIG. 3. Anomalies of the specific heat of In + 4.85 at.% Cd alloy in the region of the fct \rightleftharpoons fcc transitions, registered with an automatic microcalorimeter: a — bulky aged sample, b — aged wire sample, c — freshly extruded wire sample (the shaded area corresponds to the latent heat). The left and right halves of each figure correspond to fcc \rightarrow fct and fct \rightarrow fcc transitions, respectively.

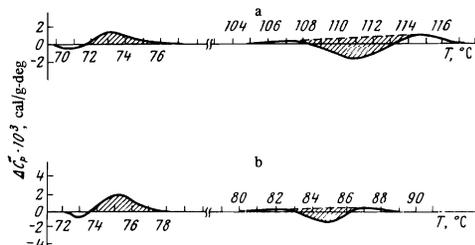


FIG. 4. The same as in Fig. 3, for the alloy In + 20.0 at.% Tl: a — unaged bulky sample, b — freshly extruded wire sample. The left and right halves of each figure pertain to the fcc \rightarrow fct and fct \rightarrow fcc transitions, respectively. The areas corresponding to the latent heat are shown shaded.

→ fct transition when either bulky or wire aged samples of the In-Cd alloy are cooled is intermittent. This is particularly noticeable with the wire sample. The curves corresponding to the reverse fct → fcc transition are smooth. A characteristic feature of the curves for the unaged alloys is the presence of secondary effects of opposite sign, which appear both in heating and in cooling. The values of the integral thermal effects corresponding to the principal peaks (shown shaded in the figures) and the secondary peaks of ΔC_p are listed in Table I.

Let us estimate the volume effects of the investigated transitions. Assuming for In + 4.85 at.% Cd a thermal effect $\Delta H = (8.6 \pm 0.7) \times 10^{-3}$ cal/g (the mean value of the thermal effects obtained in heating and cooling of an aged wire sample—Fig. 3b) and $dT/dP = (7 \pm 0.7)$ deg/kbar in accordance with the Clapeyron-Clausius equation, we find that in the fct → fcc transition the change of the volume in this alloy is $\Delta V = (0.084 \pm 0.016)$ cm³/g-atom or $\Delta V/V = (0.5 \pm 0.1)\%$. According to x-ray data^[4], the volume of this alloy at the transition point (345°K) is (15.6 ± 0.08) cm³/g-atom. For In + 20.0 at.% Tl, we have $\Delta H = (4.3 \pm 0.5) \times 10^{-3}$ cal/g (mean value of the principal thermal effects in heating and cooling for a wire sample—Fig. 4b), $dT/dP = (0 \pm 0.5)$ deg/kbar, and $V(353^\circ\text{K}) = (16.2 \pm 0.08)$ cm³/g-atom^[5]. The corresponding calculation yields $\Delta V = (0 \pm 0.04)$ cm³/g-atom and $\Delta V/V = (0 \pm 0.03)\%$.

DISCUSSION OF RESULTS

The features of the behavior of the specific heat of In-Tl and In-Cd alloys in the fct ⇌ fcc transition interval confirm the existing notions concerning the nature of these transitions as being diffusionless structure transitions of the martensitic type, the thermodynamics and kinetics of which are determined mainly by the change of an internal parameter, namely the lattice deformation, and by the fields of the internal stresses. The character of the thermal anomalies and the hysteresis of these transitions depend on the thermal history, shape, and microstructure of the samples. This dependence is seen particularly clearly when the results of the investigations of aged and freshly extruded samples are compared. The jumplike and explosive type of fcc → fct transition in the aged In + 4.85 at.% Cd alloy (Figs. 3a and 3b) is typical of the so-called “athermal” martensitic transformation. A similar jumplike process of formation of the tetragonal phase in In alloys was observed earlier metallographically^[16].

The “waviness” of the ΔC_p curves in the region of the transition, in the case of freshly prepared In-Cd

TABLE I. Integral effects of fct ⇌ fcc transitions in In + 4.85 at.% Cd and In + 20.0 at. % Tl alloys.

Alloy	Thermal effect of fcc → fct transition, 10 ⁻³ cal/g		Thermal effect of fct → fcc transition, 10 ⁻³ cal/g	
	Principal	Secondary	Principal	Secondary
In + 4.85 at.% Cd, bulky, aged (Fig. 3a)	4.2±0.4	—	4.6±0.5	—
wire, aged (Fig. 3b)	9.0±0.7	—	7.3±0.7	—
wire, fresh (Fig. c)	5.6±0.6	4.0±0.4	6.6±0.7	1.2±0.1
In + 20 at.% Tl, bulky (fresh)(Fig. 4a)	10.7±1.0	6.9±0.7	7.0±0.7	1.8±0.2
wire (fresh) (Fig. 4b)	3.6±0.1	3.5±0.4	5.0±0.5	0.9±0.09

and In-Tl alloys (Figs. 3c, 4a, and 4b) agrees with the character of the anomalies of C_p observed in^[9] for the alloy In + 28.9 at.% Tl, which experiences an fcc → fct transition in the range 70–100°K. These anomalies consist of a “smearing” of the principal effects (due to the latent heat) and the appearance of secondary effects in the immediate vicinity of the transition point. The secondary positive anomalies of the specific heat in unaged alloys, which accompany the fct → fcc transition, can be regarded as a “vestige” of the annealing of the defects and relaxation of the internal stresses, which occur when the crystal has become restructured. The negative anomalies of the specific heat, observed during cooling of unaged alloys following the release of the latent heat, are apparently due to accumulation of elastic energy in the low-temperature phase. Immediately after its formation, the tetragonal phase possesses an appreciable negative coefficient of thermal expansion along the c axis. When the temperature of the alloy In + 20.4 at.% Tl is changed by only 10–15° below the fcc → fct transition point, the axis ratio c/a increases from 1.015 to 1.020 as a result of this effect^[5]. In the case of the complex domain structure of the fct phase produced in a polycrystalline sample, an increase in the degree of tetragonality should lead to the appearance of appreciable internal stresses, which can cause a phenomenon similar to the elasto-caloric effect observed when external stresses act on the sample^[17]. The thermodynamic properties (including the thermal elasticity) of crystals in which the internal strain can be regarded as an independent thermodynamic variable, were recently discussed in^[18]. The abrupt change in the tetragonality in In-Tl alloys immediately ahead of the fct → fcc transition is the cause of one of the manifestations of the “shape memory” effect observed in these alloys.^[19]

The fcc → fct phase transition in In-Tl alloys is preceded by a phenomenon connected with the loss of stability of the cubic lattice to shear deformation. The shear modulus ($\frac{1}{2}$) ($C_{11} - C_{12}$) of the fcc phase of these alloys tends to zero near the fcc → fct transition and is characterized by an anomalous (positive) temperature coefficient^[20,21]. This phenomenon agrees with the observed crystal geometry of the fcc → fct transitions in indium alloys, the principal element of which is a shear along the system (110) $\langle 1\bar{1}0 \rangle$ ^[8,16].

Shear deformation plays the principal role in fcc → fct phase transitions. It leads to formation of a multidomain structure made up of crystallographic twins that are conjugate along the {110} planes. The evolution of the internal stresses during the course of formation of the domain structure exerts an essential influence on the thermodynamics of the transition and severely limits the region in which results obtained with specific samples can be regarded as general. By regarding the shear deformation $\epsilon = (\frac{2}{3})(c/a - 1)$ as the only transition parameter and expanding the free energy near the transition point in powers of ϵ (confining ourselves to second-order terms), we can obtain an estimate for the latent heat where $A = (\frac{3}{4})(C_{11} - C_{12})$, and $\epsilon(T_m)$ is the shear deformation at the transition point T_m . For the alloy In + 20.0 at.% Tl near the transition point we have $dA/dT \approx 7 \times 10^7$ dyn/cm² deg^[20], $T_m = 350^\circ\text{K}$, and $\epsilon(T_m) = 1 \times 10^{-2}$ ^[5]. Consequently, for this alloy the latent heat of the transition should be $\sim 7 \times 10^{-3}$ cal/g. The estimate of $\Delta U(T_m)$ is in good agreement with the experimental values (see the table).

Since the energy effects of the fcc \rightleftharpoons fct transitions in indium alloys are small and depend in many respects on the "supercooling" or "superheating" of the transition (especially in view of the anomalously strong change of c/a with temperature), and also on the internal-stress fields, only the signs and orders of magnitude of the quantities are meaningful. This applies equally to the values of the volume changes calculated from the Clapeyron-Clausius equation and to the value of the jump of c/a at the transition point, as well as to other characteristics of the transitions. The foregoing remark apparently holds true also for other systems with phase transitions that are structurally analogous (AuMn, CoO, V_3Si , Nb_3Sn , etc.).

It follows from the experimental data obtained in the present paper that the formation of the more symmetrical fcc phase in the In-Cd alloys in the fct \rightleftharpoons fcc transition is accompanied by an increase in the volume (the sign of the volume effect is fully determined by the sign of the derivative dT/dP). The results of pycnometric measurements^[7], according to which the volume of an In-Cd alloy decreases in an fct \rightarrow fcc transition, does not agree with the slope of the plot of the transition temperature against pressure, and is incorrect both with respect to the magnitude and with respect to the sign of the measured effects. Plots of the specific volumes of In-Cd alloys against temperature and concentration, obtained as the result of precision x-ray diffraction investigations^[4], reveal regular spikes of the experimental points along the fct \rightarrow fcc transition curve, which also indicate that the fcc phase has a higher specific volume at the transition point.

On the basis of the results we can advance certain ideas concerning the virtual fct \rightarrow fcc transition in pure indium. It is known that the stability of the fct structure of indium decreases with increasing temperature. This becomes manifest both in a lowering of the ratio of the tetragonality axes of the indium^[1,2] and in an anomalously strong decrease, following heating, of the elastic-constant combinations that determine the stability of the fct structure of indium to shear, namely $C^1 = (C_{11} - C_{12})/2$ and $C^{11} = (C_{11} + C_{33} - 2C_{13})/4$ ^[22]. According to the data of Chandrasekhar and Rayne^[22], the modulus C_1 of pure indium decreases in the temperature interval 4.2–300°K by a factor of three, whereas for fcc aluminum the change of the modulus C^1 in this temperature interval is only 10%. At atmospheric pressure, the temperature of the virtual fct \rightarrow fcc transition in pure indium, obtained by extrapolating the phase-equilibrium lines in its alloys^[1,4,10], lies some 200–250° above the melting point. It was assumed in a number of papers^[23,24] that the point of the virtual fct \rightarrow fcc transition in pure indium can become lower when hydrostatic pressure is applied, until the equilibrium boundary of the solid phases intersects the melting curve $T(P)$. This assumption, however, was not confirmed by experiment^[23,25-28]. That there is no fct \rightarrow fcc transition at room temperature is evidenced by a direct x-ray structure investigation of indium carried out up to ~ 300 kbar^[27,28], which showed that the ratio c/a remains larger than unity in the entire pressure interval, and even increases at pressures 0–100 kbar. The experimental data of^[27] agree with estimates obtained for the linear-compressibility coefficients of pure indium from its elastic moduli^[20,22].

It is more logical to assume that the fcc modification of pure indium can become stable at negative pres-

ures. This conclusion agrees with the positive volume jump in the fct \rightarrow fcc transition in In-Cd alloys, which indicates that, at least in these alloys, the specific volume of the cubic phase is not lower than the specific volume of the tetragonal phase, but higher. From this point of view, the fct \rightarrow fcc transition in the In-Tl system can be attributed to an increase in the volume of the tetragonal indium when alloyed with thallium^[29,30], which is analogous to applying negative pressure to the indium. It is impossible to explain the fcc \rightarrow fcc transition in the In-Tl system as being due to a decrease in the average electron concentration by alloying, as in the case of In-Cd or In-Hg, since thallium is isovalent to indium.

In conclusion, let us examine the effects of the change of volume in the fct \rightarrow fcc transition process in indium alloys on the thermodynamics of these transitions. A number of attempts have been made^[11,12] to establish a correlation between the tetragonal distortion of the crystal lattice and the electronic structure of an indium-based alloy by using the model of almost-free electrons, which agrees well with the experimental data for pure indium. It was assumed that the deformation of the band is produced by a shear without change in volume, and that the ratio c/a of the lattice parameters of the tetragonal indium alloys is determined by the concentration of the free carriers. The equilibrium values of c/a were calculated from the condition that the thermodynamic potential be at minimum, with allowance for the changes $\delta E_{\text{electr}}(\epsilon_{ij})$ of the electron energy following deformation and $\delta E_{\text{elast}}(\epsilon_{ij})$ of the elastic shear energy of the crystal lattice. The calculations can explain semiquantitatively the change of c/a in indium alloys with changing free-carrier concentration, and also predict the concentration regions where the tetragonal structures with $c/a \geq 1$ and $c/a \leq 1$ can be stable. From diagram 12 of^[12] it follows that $\delta E_{\text{electr}}(\epsilon_{ij}) \approx 2.0 \times 10^{-1}$ cal/g on the fcc \rightleftharpoons fct phase boundary of In-Cd alloys.

Let us estimate the contribution of the volume effect to the energy balance of the fct \rightleftharpoons fcc transition. To account for the change of volume in the fct \rightleftharpoons fcc transition in In-Cd alloys, it is necessary to take into account the additional elastic energy

$$\Delta U(T_m) = -T_m \epsilon^2 (T_m) dA / dT,$$

At $\eta = \Delta V/V = 0.005$ for the In-Cd alloy, and using the fcc-alloy elastic moduli given in^[21] (the modulus combination $C_{11} + 2C_{12}$ experiences no anomaly in the region of the phase transition), we obtain $\delta E'_{\text{elast}} = 1.4 \times 10^{-1}$ cal/g. Consequently, the elastic dilatation energy in In-Cd alloys, which was not taken into account in^[12], is close in order of magnitude to the change of the electron energy, and should be taken into account in calculations of the stability of the fct and fcc structures in alloys of indium with cadmium. The volume changes should also be taken into account in crystal-geometry calculations of fcc \rightarrow fct transition in In-Cd alloys. These changes may be essential in the determination of the habit, domain-wall orientation, and domain composition of the tetragonal phase. For the In-Tl system, the volume changes in the fcc \rightarrow fct transition are less than the measurement errors and can apparently be neglected both in the energy calculations and in discussion of the crystal geometry of the transition.

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