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FEATURES OF THE BEHAVIOR OF THE ORDER PARAMETER IN THE SUPERIONIC CRYSTAL LAF_3

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ABSTRACT

The temperature behavior of the physical quantity η, called the order parameter and determining the degree of disordering of the lattice of an ion-conducting material is analyzed. As an object of study, we took the LaF_3 superionic crystal from an extensive class of materials in which the transition from the dielectric to the superionic phase is determined by the disordering of one of the sublattices, which is smeared in a certain temperature range, and is not accompanied by a significant rearrangement of the crystal lattice structure. It was shown that at the critical point T_c = 263 K, the disordering of the anionic sublattice LaF_3 does not end, but continues at higher temperatures.

KEYWORDS: *Superionic Conductors, LaF_3 Nanocrystal, Internal Motion*

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INTRODUCTION

The interest shown in recent decades in the study of disordered solid-state systems is determined by the formation at the junction of molecular physics and solid-state physics of a new direction associated with high internal motion in the lattice of a solid at temperatures significantly lower than the melting temperature of the material. Moreover, the phenomenon of internal motion is realized in a rather wide class of substances, which includes solid-state materials with anomalously intense movement of ions in one of the sublattices.

Such materials are called superionic (SI) conductors or solid electrolytes. The lanthanum trifluoride under study also belongs to such materials, in which the phase transition (phase transition) from the dielectric (DE) state to the highly conductive (HC) is smeared in a certain temperature range. The anionic sublattice of the LaF_3 crystal consists of three types of fluorine ions, which differ structurally — the F_1 ions (≈ 70% of all anions), F_2, and F_3. The elementary hexamolecular cell contains 18 fluorine ions: 12 F_1, 4 F_2 and 2 F_3.

In studies of the lattice structure of tysonite-like crystals, it was assumed that the LaF_3 crystal can crystallize in at least two modifications with space groups $P\bar{3}c1$ and $P6_3/mcm$ [1, 2]. The first of them corresponds to a low-symmetric anionic environment and the second corresponds to a more symmetric one, which occurs at higher temperatures.

As is known (Figure 1), in the unit cell, lanthanum ions form triangles at Z = 0.25 and 0.75, deployed by a C_6 screw operation at 60° relative to each other. In this case, 12 F_1 ions are displaced from the vertical plane passing through

the lanthanum ions by 0.042 nm (0.059 lattice constant a), and four F_2 ions are displaced by 0.046 nm (0.064 s) from the anion-cation plane. The F_3 ions are located exactly in the centers of the triangles composed by lanthanum ions with coordinates (0,0,1/4) and (0,0,3/4). It is clear that in accordance with the trigonal symmetry $P\bar{3}c1$, both the F_2 ions and the F_3 ions are located on the third-order local axes C_3

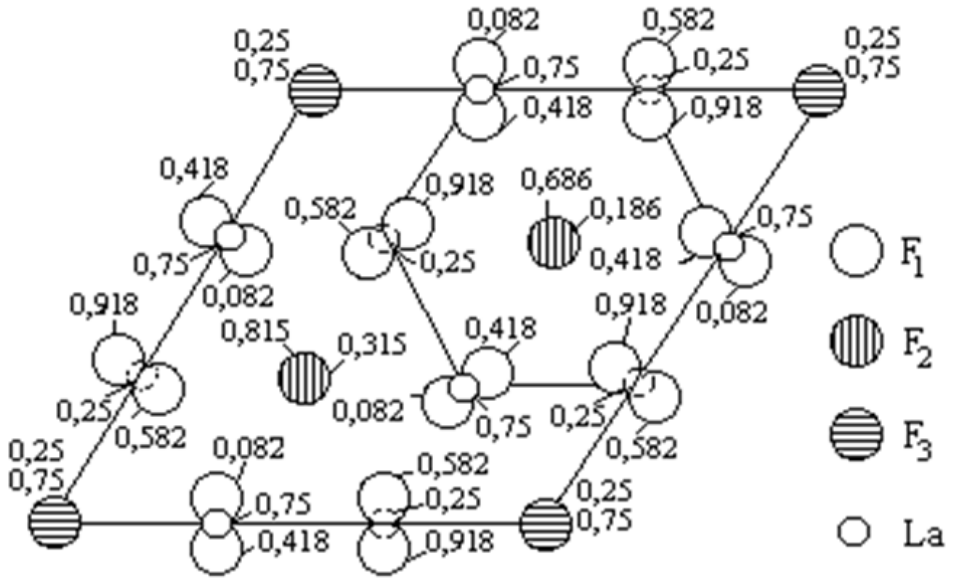

Figure 1: The Projection of the LaF_3 Unit Cell onto the XY Plane [1].

An order parameter η may be of some combination of characteristic quantities that determine phase transformations in a given material, provided that in the low-temperature region (for the low-temperature phase), the parameter is $\eta = 1$, and for the high-temperature phase, $\eta = 0$. For transitions of the first, it is almost always possible to make a combination of characteristic parameters that satisfies this condition. As will be shown below, for a wide range of SI materials, this condition is far from always satisfied. Next, we analyze the temperature behavior of the order parameter η, which determines the degree of disordering of the lattice of the SI material with diffuse phase transitions.

RESULTS AND DISCUSSIONS

As is known, for the SI crystal of LaF_3, the maximum fraction of disordered fluorine ions is described by the value 0.5 $N_2/N_1 = 3/18 \approx 0.17$. Here, $N_1 = 18$ is the total number of fluorine ions in the hexamolecular cell, $N_2 = 6$ is the total number of internodes in it, of which only half can be occupied by fluorine ions [3]. It follows that with the participation of internodes, 17% of F_1 ions move and with the participation of nodal vacancies 83%. With this in mind, the parameter for the LaF_3 crystal can be taken as the parameter

$$\eta = (N_1 - 0.5\, N_2)/N_1. \quad (1)$$

As already noted, the disordering of the anionic sublattice is mainly determined by the “melting” of the F_1 ion sublattice. Therefore, we will further consider the order parameter η corresponding to disordering of the F_1 ion sublattice.

From Figure 2, it can be seen that $T_o = 152$ K in Fig. 3a corresponds to the temperature at which the disordering (“melting") process of the F_1 sublattice begins. Figure 2 also shows that at the point $T_c = 263$ K, the process of disordering

of the F_1 sublattice does not end, but continues to temperatures ≈ 280–300 K. Moreover, only one-third (33%) of the maximum possible fraction of disordered F_1 ions is disordered at the point T_c [3].

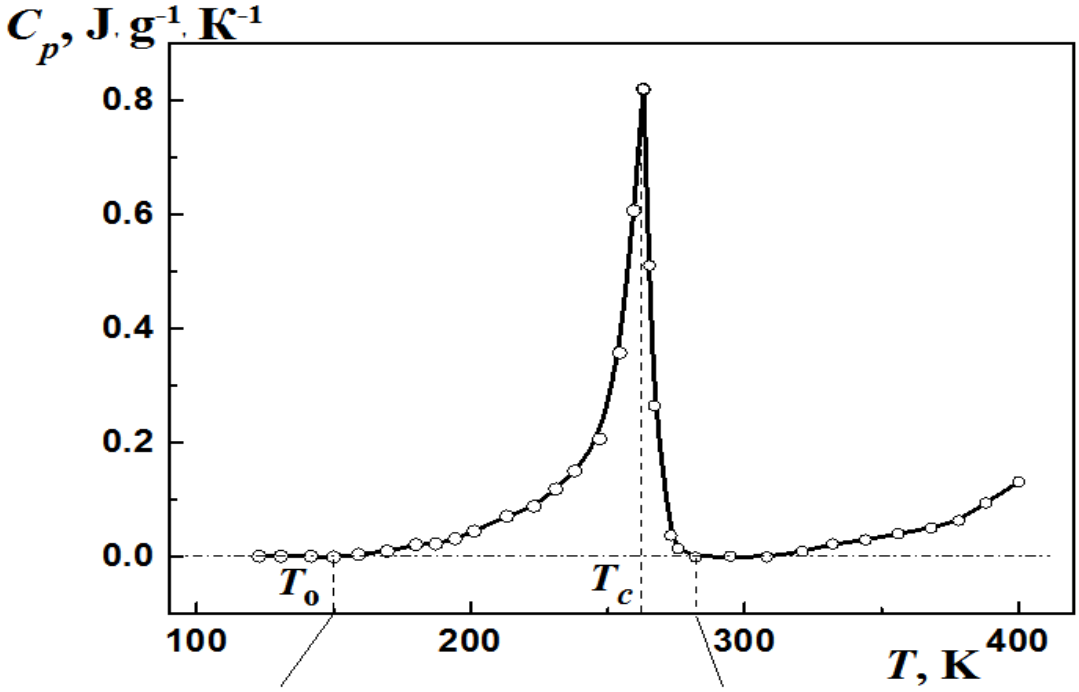

Figure 2: Temperature Dependence of Excess Heat Capacity C_p LaF_3 Crystal [4, 5].

It follows from this that the traditional approach to determining the critical point T_c as a certain temperature that "separates" two (or more) phases of the state of matter in the case of an SI crystal LaF_3, when only partial "melting" of the lattice takes place, is not universal and requires special consideration.

At the same time, relation (1) and with it also Fig. 3(a) illustrates well the fact that in the temperature range $T <$ 152 K the structure of the LaF_3 crystal does not undergo any changes (a straight line $\eta = 1$, similar to the line in Fig. 3(b) for structural phase transitions of the first kind). Only with the beginning of the process of disordering of the lattice at the point T_o = 152 K and an increase in the fraction of mobile fluorine ions does the curve η (T) begin to take values less than 1. The value η = (1–0.17)/1 = 0.83 shows the maximum fraction of disordered fluorine ions (at $T \geq T_c$), or a kind of "degree of order" in the most disordered sublattice F_1 (although it is clear that all its ions are involved in the "melting" of the anion sublattice).

Meanwhile, at any random time (in the temperature range $T \geq T_c$), the number of disordered fluorine ions on average does not exceed 17% of the total number of fluorine ions in the LaF_3 lattice. In connection with the foregoing 1/3 of this number is disordered at the point T_c (approximately 5.5–6%), as shown in Fig. 3(a) for $T = T_c$ = 263 K as a value of the degree of order $\eta \approx 0.94$. It is clear that in this case, the "order fraction" in the F_1 sublattice increases from 0.83 to 0.94. It is clearly seen that in the temperature dependence of the order parameter η (T) for the phase transition in the LaF_3 crystal, both signs of the dependence η (T), which are characteristic of phase transitions of the first kind and signs of the dependence η (T) for transitions of the second kind are combined.

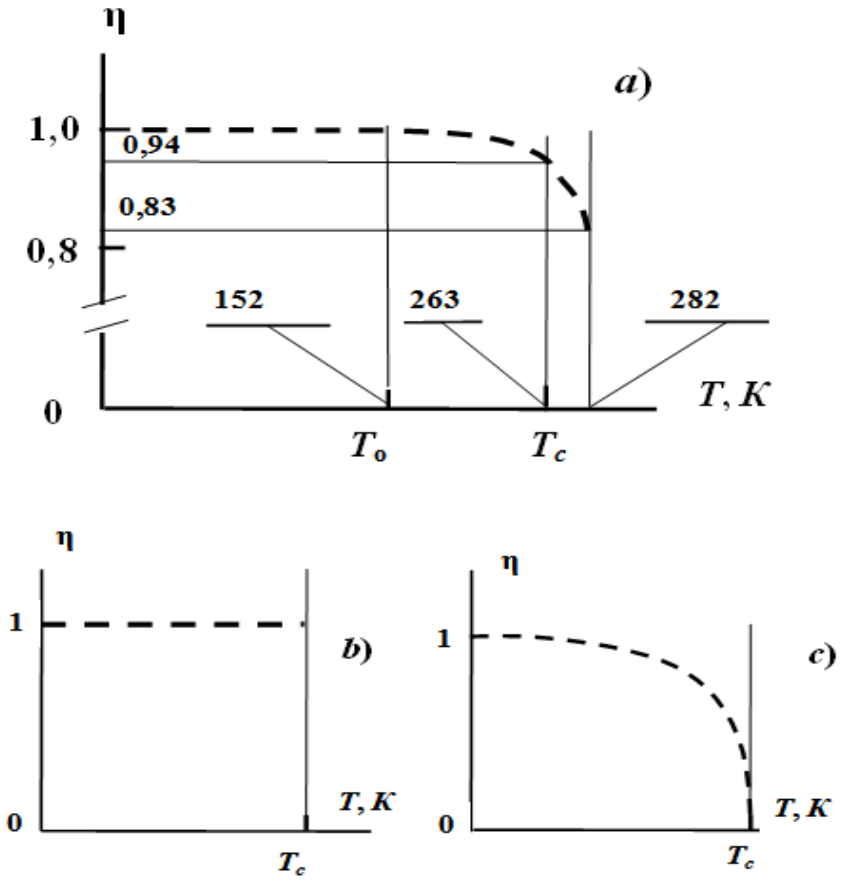

Figure 3: Temperature Dependences of the Order Parameter *H* for Phase Transitions of the First Kind Close to Transitions of the Second Kind — by the Example of an SI Crystal LaF_3 (A), Transitions of the First Kind (B) and Transitions of the Second Kind (C).

Thus, the order parameter η for the LaF_3 crystal, written in the form (1), really shows the temperature dynamics of the "new quality" - the "melting" (disordering) of the F_1 ion sublattice - both in the low-temperature phase (at $T < T_c$) and at relatively high temperatures (at $T \geq T_c$). For the case of the LaF_3 crystal, it is clear that the order parameter η cannot take the value zero, which would correspond to the "melting" of the entire anionic sublattice (for SI crystals with smeared phase transitions, this is practically unattainable at temperatures well below the melting temperature of LaF_3).

We also note that when calculating the parameter η according to (1), it was assumed that in the SI phase, the populations of nodes and internodes by fluorine ions F_1 are the same and equal to 1, although in reality, the populations of internodes are slightly less than 1 [6]. In other words, the number of disordered fluorine ions was equal to the number of equivalent internodes. It is clear that in the general course of the temperature dependence of the curve η (T) in Fig. 3 this has almost no effect.

For structural phase transitions of the first kind, the order parameter η in the general case includes various lattice translations, by changing, which becomes possible to change the symmetry of the initial lattice, for example, the transition for an AgI crystal from a hexagonal lattice to a body-centered cubic α-AgI structure in SI phase. Fig. 3(b) shows that for a first-order phase transition, the order parameter η can take only two values: 1 (for the region $T < T_c$) and 0 at $T \geq T_c$. Thus, at the point T_c for a first-order phase transition, the order parameter η undergoes a jump in its value as does a number of other characteristic parameters, such as the volume of the disordered part of the lattice, its entropy, etc.

Figure 3(c) shows the behavior of the order parameter for the general case of a phase transition of the second kind (regardless of the type of its representation). It is clearly seen that with such a transition, a new quality (superfluidity, ferromagnetism, superconductivity, etc.) arises immediately in the entire volume of the considered system of particles — though at first in "small quantities". With increasing temperature, a new quality increment occurs (for example, microscopically small displacements of ions of a certain type) and at $T = T_c$, small displacements reach their maximum values (without noticeable effect on the symmetry elements of the initial structure) and the parameter η takes a value of zero, which corresponds to the largest "disorder" in the array of particles under consideration.

For phase transitions of the first and second kinds, the analytical form of the parameter η is not given in the paper, since several versions of this representation are possible. In our case, it was much more interesting and more important to show the analytical form of the parameter η for the case of an SI crystal LaF_3 with diffuse phase transitions, for example, in the form (1).

CONCLUSIONS

The results obtained in this paper allow us to draw the following conclusions:

On the example of the lattice of the LaF_3 crystal, the relative fraction of internodes (≈ 0.17) participating in the disordering of the lattice (three internodes per 18 fluorine ions in a hexamolecular cell) was established in the SI phase in the temperature range $T \geq T_c$), the average number of disordered fluorine ions does not exceed 17% of the total number of fluorine ions in the LaF_3 lattice. At the same time, only one-third of this number is disordered at the point T_c,, i.e., approximately 5.5–6%, which corresponds to a degree of the order of $\eta \approx 0.94$ for $T = T_c = 263$ K it was shown that 83% of fluorine ions is transferred with the participation of nodal vacancies and only 17% - with the participation of internodes.

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