

Dynamic structural transition in the superionic conductor $\text{Na}_5\text{RESi}_4\text{O}_{12}$

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(Submitted 20 November 1991)

Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 1, 48–51 (10 January 1992)

Experiments have been carried out on Eu^{3+} probe ions in the superionic conductor $\text{Na}_5\text{RESi}_4\text{O}_{12}$ near 400 K by the method of fluorescence spectroscopy. It is concluded from the results and from a comparison of these results with existing structural data that a restructuring of the material which occurs near 400 K is a “dynamic structural transition” of an intermediate type—something between first-order and second-order in Landau’s classification of phase transitions.

1. Several studies of processes in superionic conductors have used laser spectroscopy of luminescing ions, serving as probes. This research is reviewed in Ref.1. Because of the particular way in which the level splitting of the luminescing Gd^{3+} ion depends on the positions and motion of the mobile cations, it is possible to extract information on processes in the “molten sublattice” of a superionic material. In the present experiments we used Eu^{3+} ions as probes in $\text{Na}_5\text{RESi}_4\text{O}_{12}$ single crystals. The level scheme of this ion is more complex than that of the Gd^{3+} ion, so more-detailed information can be obtained.

Specifically, we studied the luminescence spectra corresponding to the transition ${}^5D_0 \rightarrow {}^7F_1$ over the temperature range 100–500 K and the processes which occur in the mobile sublattice of conduction ions in this temperature range. It is in this temperature range that an insulating crystal converts into a material with a high ionic conductivity (0.1 mho/cm), sufficient for technical applications.²

The object of this study, $\text{Na}_5\text{RESi}_4\text{O}_{12}$, goes through no clearly expressed phase transitions in its superionic state. This circumstance is consistent with the low dimensionality of the conductivity of this material (which consists of a set of weakly coupled one-dimensional channels crossing the crystal in three directions). Some data indicate that changes of some sort occur in the mobile sublattice in this temperature range, against the backdrop of a nearly constant rigid sublattice.³ The possibility of learning about the processes by which the superionic state is reached, in a situation in which these processes are not masked by accompanying changes in the rigid sublattice, is of major interest in our case.

The $\text{Na}_5\text{RESi}_4\text{O}_{12}$ single crystals were grown by a hydrothermal method. The luminescence was observed in a plane grown perpendicular to the optical axis of the crystal, in a 180° geometry. The experimental apparatus has been described in previous papers. The excitation in these experiments corresponded to the energy of the ${}^5D_0 \rightarrow {}^7F_0$ transition of the europium ion.

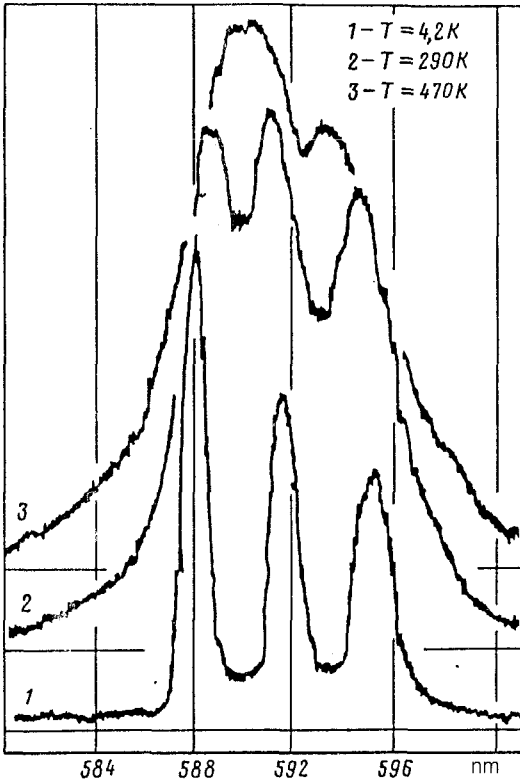


FIG. 1. Overall luminescence spectra of Eu^{3+} ions in $\text{Na}_3\text{RESi}_4\text{O}_{12}$ single crystals at various temperatures.

2. The positions of the luminescence spectral lines and their temperature dependence found in these experiments are unambiguous evidence that the lattice of the superionic material undergoes at least a partial restructuring in this temperature range. Figure 1 shows several typical spectra; Fig. 2 shows data on the positions of the lines over the entire temperature range. The first thing we note on the curves in Fig. 1 is a clearly expressed shifting and merging of lines. These are not spurious effects, i.e., not a blurring because of a line broadening. In Fig. 2 we can extrapolate the changes in the positions of individual lines and determine the point at which they merge. It is near 400 K. The dashed line in Fig. 2 shows the position of the barycenter of the given multiplet. The absence of changes (the absence of any significant "nepheloxetic" shift) indicates that no changes occur in the distances between the luminescing probe ion and the nearest coordination sphere of the oxygen ligands. This result supports the existing x-ray structural data, which indicate that no structural transitions occur in the rigid sublattice.

A change in the number of lines in a multiplet is direct evidence of a change in the symmetry of the lattice site occupied by the luminescence Eu^{3+} probe ion. Since the first coordination sphere is approximately a regular octahedron and remains essential-

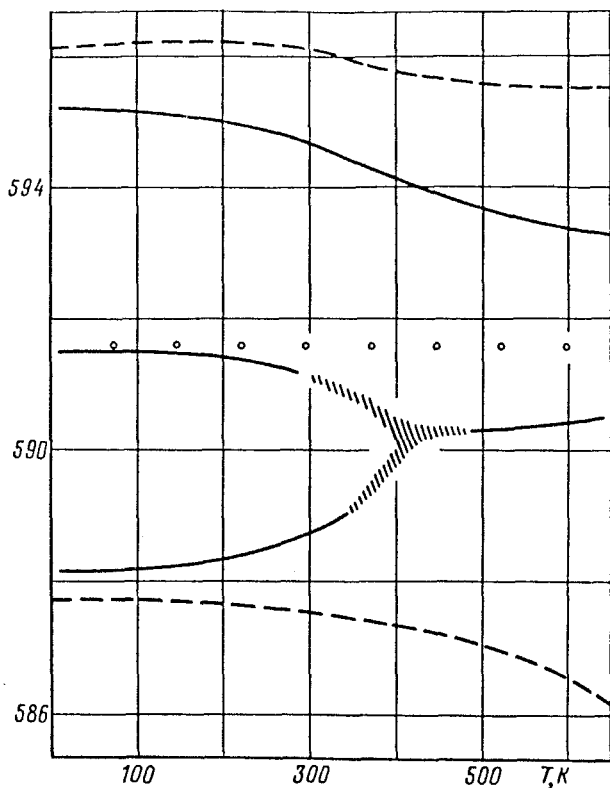


FIG. 2. Temperature dependence of the positions of lines in the spectrum (Y axis; the wavelengths are in nanometers) near the dynamic structural phase transition.

ly unchanged as the temperature is varied, the reason for the observed changes in symmetry must be sought in changes in the second coordination sphere. In this second sphere, changes in population occur because of a thermal activation of ionic conductivity processes. A decrease in the number of lines in a multiplet with increasing temperature corresponds to an increase in the symmetry of the site. Changes of this sort can evidently be expected as a consequence of the attainment of a more nearly uniform average distribution of cations in the lattice, because of their intense motion.

Additional data for determining the symmetry were obtained in an analysis of the luminescence spectra on another transition ${}^5D_0 \rightarrow {}^7F_2$. This multiplet has five lines at 200–300 K; above 500 K, four spectral lines were observed. According to the known symmetry properties of the $4f$ shell of the Eu^{3+} ion, we can thus interpret the change in the symmetry of the site as an increase in the symmetry to tetragonal from some lower symmetry. The particular way in which the europium levels split rules out a more-detailed determination of the symmetry of the low-temperature phase on the basis of the existing data.

A few conclusions about the nature of the restructuring of the lattice near 400 K can be drawn from a comparative analysis of these results and the results of Ref. 3. In each case, the quantity characterizing the deviation from the high symmetry (the

magnitude of the splitting in our case; the intensity of an informative reflection in Ref. 3) falls off gradually over an interval of about 70 K to the point of the transition to the high symmetry. A behavior of this sort—such that the material in the low-temperature vicinity of the transition point is physically indistinguishable from the high-temperature phase—is characteristic of a second-order phase transition according to Landau's theory.⁴

3. These arguments do not, however, take account of all the distinguishing features of the case at hand, and to conclude that a second-order phase transition is occurring would be to oversimplify. In each method—that of the present study and that of Ref. 3—the information found pertains to an average density of mobile cations. In Ref. 3, the averaging was over many lattice constants and over the duration of the experiment, while in the present study the averaging is over the neighborhood of the probe ion and over the lifetime of the excited state.

On the other hand, the instantaneous positions of the particles in the neighborhood of the luminescing probes could not give rise to any high-symmetry configuration of the ions (other than C1). This point is determined unambiguously by the particular way in which the sites are positioned in the lattice and by the small, countable number (3 or 4) of mobile ions which could occupy the second coordination sphere of the RE ion without causing a serious deviation from electrical neutrality. The relatively high symmetry types which follow from the spectroscopic data are a consequence of the circumstance that the probe ion detects the average distribution of the mobile cations.

These mobile ions, however, are fairly heavy, so they conform to arguments about classical particles to a large extent. The blurring of the average density, with the formation of spatially symmetric average-density functions, could not be due to wave properties of the particles in this case. It is instead the result of an intense motion of the conduction ions. What we are actually seeing here is yet another manifestation of “dynamic averaging.” It follows that the spatial restructuring of the lattice, which can be identified as second-order transitions in our case, according to the structural and spectral data, is, to the same extent, the result of a transition to particle motions of different types. A transition to motions of different types would unavoidably require an additional absorption of energy by the system. In other words, this transition should be a first-order transition and should be characterized by a latent heat of transition.

In the case of superionic conductors, this transition is a transition from local motions to translational motions. It is for this reason that an effective averaging is possible, and fairly symmetric average distribution functions can be found. A change of this sort in the nature of the motion is evidently a microscopic analog of melting or sublimation (while the “background,” i.e., the rigid sublattice, is conserved). Consequently, several arguments indicate that the restructuring in $\text{Na}_5\text{RESi}_4\text{O}_{12}$ should be classified as an intermediate case, somewhere between first-order and second-order phase transitions.

To find further information on the nature of this restructuring in the lattice, we measured the specific heat of this material (using ceramic samples for this purpose) in the vicinity of the presumed transition, 300–470 K. For these measurements we used a

Cetaram DSC-111 scanning microcalorimeter. Against the background of a general increase in the specific heat with increasing temperature in this temperature range, we can see no more than a slight deviation from a monotonic $C(T)$ curve in the vicinity 350–420 K (the deviation is on the order of 1%). There are no hints of heat evolution in this range. The absence of any significant anomalies in the thermal characteristics in the face of the obvious, large change in the local symmetry of the position of the RE ion cannot provide further information on the nature of the transition. It merely indicates that the restructuring involves only a fairly small fraction of the crystal lattice.

The situation examined by us here is not exceptional. Transitions which cannot be clearly identified as either first-order or second-order phase transitions have been seen elsewhere. In particular, a “weak” heat evolution is observed in superionic conductors. The term “weak first-order phase transition” has been used.⁵

In general, the data and arguments presented here explain the microscopic reasons for the appearance of effects of this sort in our case. We think it appropriate to label these effects “dynamic structural transitions.”

We wish to thank E. A. Uksha for furnishing the ceramic samples and A. A. Kosyĭ for carrying out the thermal measurements.

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Translated by D. Parsons