Eu³⁺ probe-ion spectroscopy in the superionic conductor Na₅YSi₄O₁₂: effects due to the dynamics of the molten sublattice

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Luminescence of Eu³⁺ ions was investigated at the temperatures of the transition of Na₅RESi₄O₁₂ from an insulator crystal to a superionic conductor. An anomalously strong decrease of the multiplet splitting and changes in the numbers of lines in the multiplets corresponding to structural transitions with symmetry change were observed. The observed anomalies of the spectral characteristics are interpreted as the result of changes, accompanying the temperature rise, in the sublattice of the mobile Na⁺ cations. It is proposed that the main mechanism of the observed effects is dynamic averaging of the cation configurations.

INTRODUCTION

We have investigated the luminescence of rare earth ions in the superionic conductor Na₅RESi₄O₁₂ in a series of studies. This direction of research was stimulated by a unique combination of advantages of luminescence methods: Various versions of these methods are sensitive to the structure and composition of the material and also to the dynamics of the particles which make up the material. Interrelated problems involving structure and dynamics arise in research on superionic conductors, so these methods are particularly useful in this case.

The results of experiments carried out on this material by means of luminescent Gd³⁺ ions are summarized in a review.[1] The Eu³⁺ ion is known to have a quite different system of levels. From the spectroscopic standpoint it is a "complement" to the Gd³⁺ ion: In general, the information obtained from research on the spectra of these ions is effectively complementary.[2]

In this material the rare earth (RE) ions occupy regular octahedral sites in the lattice (in this case the Eu³⁺ ions partially replace optically inactive Y³⁺ ions). The dependence of the optical spectra of the RE ions on the processes which occur in the sublattice of mobile cations results from the effect of the electric field of the mobile Na⁺ cations in the second coordination sphere of the rare earth ion on the $4f$ levels of this ion.

The results of our study by Eu³⁺ spectroscopy of the material at low temperatures are described in Ref. 3. The primary result of this study was the observation by the spectroscopic method of a selective excitation of a latent discrete nature of the spectra. This discrete nature was interpreted as resulting from the existence of mobile cations in the sublattice against the background of an apparent disorder and a small number of stable local cation configurations. The specific positions of the cations in the configurations were reconstructed. The relative probabilities for the various configurations were calculated on the basis of the known structural data. The positions of the lines in the spectra of the Eu³⁺ ions were calculated from the types of configurations found for the cations forming the second coordination sphere of the luminescent RE ions. The good agreement between the theoretical and experimental positions of the lines served as confirmation of the validity of that reconstruction of the configurations.

To the best of our knowledge, these are the first data of this sort on the latent structural nature of the sublattice of mobile ions for superionic conductors. All that had been available earlier consisted of predictions of the existence of preferred configurations on the basis of numerical simulations.[4]

An unusual combination of order and disorder is only one characteristic feature of superionic conductors. Another, and possibly more important, is the anomalously high mobility of the constituent particles. It should be noted that the mobility of the ions in the conducting sublattice is such that the classical ideas regarding a sublattice and the positions of particles in it (with respect to the mobile ions, of course) have little bearing on superionic conductors outside the low-temperature region. A fairly good picture of this situation is shown in Fig. 1, which is a series of density maps of mobile cations in the lattice of the compound Na₅RESi₄O₁₂ which we have studied.[5] On the first of these maps, which corresponds to a temperature of 110 K, we can clearly see regions of increases in the probability density corresponding to the "sites" of mobile ions. On the following maps, as the temperature is increased, the distinct sites spread out, some of them disappear completely, and the probability density in the elevated-density regions decreases substantially in comparison with the average level. Under these conditions the situation becomes very reminiscent of that in a liquid, in which it is not possible to distinguish regular positions of the neighbors in the nearest neighborhood of a probe ion, but there is a most probable radius to the nearest neighbor, and there is a coordination number.

It is not possible at the outset to predict just how an activation of motions will affect the spectra of the luminescent ions which are part of the lattice. For two limiting cases (a solid and a liquid) which are prototypes of superionic materials the motion leads to directly opposite results: In the former case the spectral lines broaden, while in
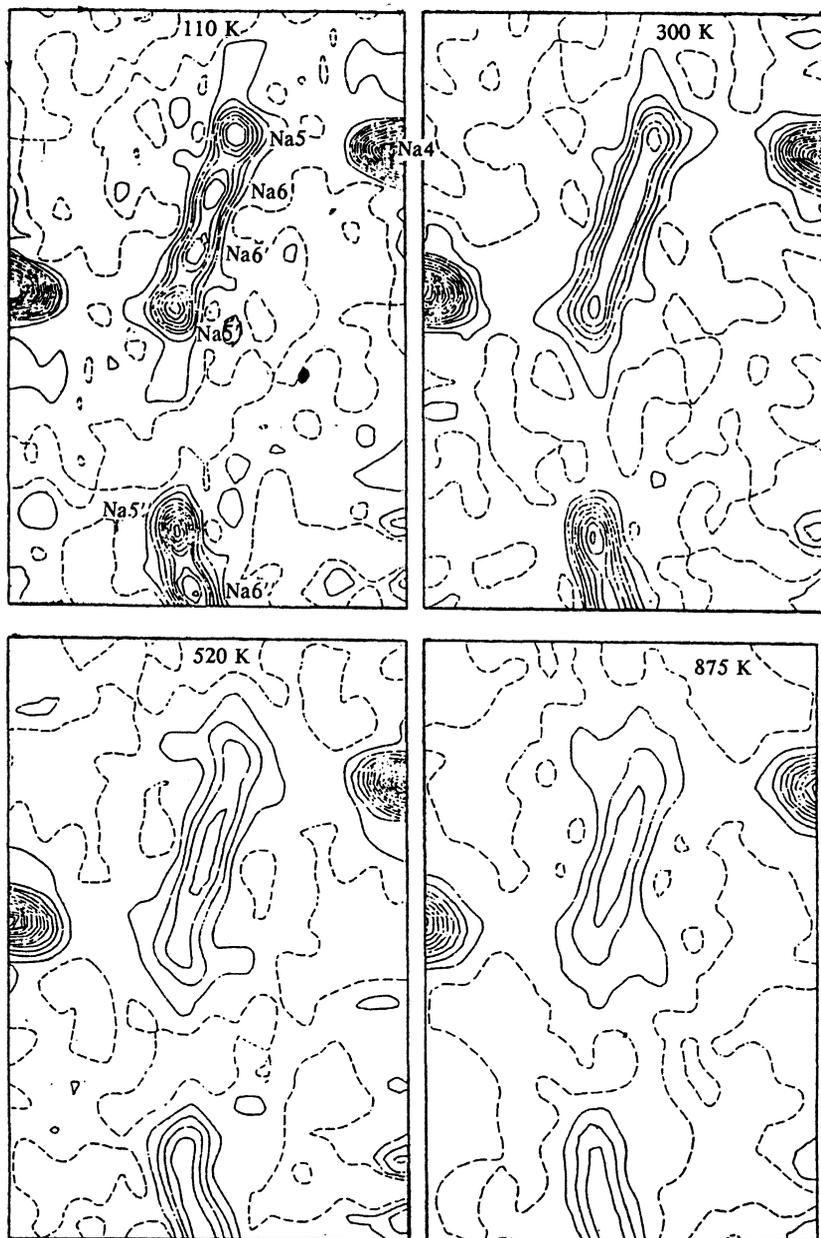
FIG. 1. Maps of the density of conduction cations in the crystal lattice of the superionic conductor $Na_5RESi_4O_{12}$ (Ref. 5). The regions of elevated density which can be seen are the positions of mobile Na^+ cations. The cross section of the lattice passes through the crystallographic sites Na4, Na5, Na6, Na6', Na5' and Na4', which constitute a conductior. channel. The sites are labeled on the map for the temperature of 110 K, at which the sites can be seen most clearly.

the latter they narrow. In addition, the splitting in a crystal field disappears in the latter case. Questions of this sort are of fundamental importance. They have not been raised previously, since it is only just recently that superionic conductors have caught the attention of spectroscopists. It is this aspect of the situation—the effect of the kinetics of the mobile ions on the spectra of luminescent lattice ions— which is the subject of the present study.

EXPERIMENTAL RESULTS

The experimental apparatus and procedures are described in detail in Ref. 3 and elsewhere. The luminescence was observed from a plane which was ground perpendicular to the optic axis of the crystal, in a 180° geometry. We assume that the basic characteristics of the luminescence of the Eu^{3+} ion are known,[2] at least to the minimum extent necessary from Ref. 3.

The temperature dependence of the positions of the lines was studied over the broad range from 4.2 to 700 K. Figure 2 shows the general shape of the spectra for the $^5D_0 \rightarrow {}^7F_1$ transition for several temperatures in this range. These curves clearly demonstrate that the changes in the positions of the lines are not small; they are instead comparable in magnitude to the intrinsic splitting of the multiplet. In addition, a change in the number of bands can be seen clearly in these spectra.

Figure 3 shows summary data on the positions of the lines of the $^5D_0 \rightarrow {}^7F_1$ multiplet of the Eu^{3+} ions for various temperatures; Fig. 4 shows corresponding results for the $^5D_0 \rightarrow {}^7F_2$ multiplet. The dots are the centers of gravity of the multiplets, and the dashed curves are the positions of the half-heights of the lines (as a rule, for the outermost lines of the multiplets). The hatched region corresponds to a coalescence, in which the individual lines can be distinguished only within a substantial error.
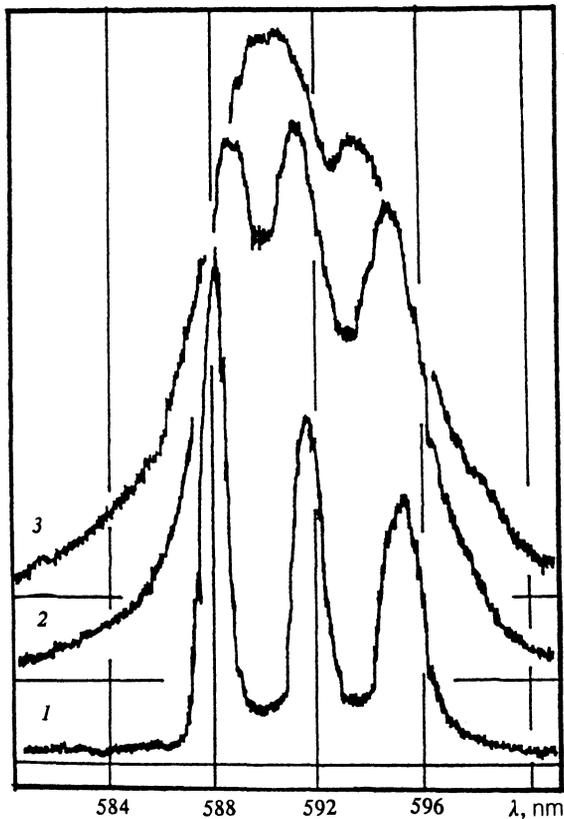
FIG. 2. Luminescence spectra for the $^5D_0 \rightarrow {}^7F_1$ transition of the Eu^{3+} ion: nonselective excitation at various temperatures. 1—$T=4.2$ K; 2—$T=290$ K; 3—$T=470$ K.

The general behavior of the lines in all the multiplets is similar to the temperature dependence which has been observed in research on the luminescence of the Gd^{3+} probe ion: In all cases the effective splitting decreases by some tenths. Note that the centers of gravity of the two multiplets remain in essentially the same positions (as they do in the case of gadolinium). This result means that the extent to which the wave functions of the RE ions and the ligands overlap remains constant. This conclusion in turn implies that no changes occur in the rigid sublattice.

So substantial a decrease in the magnitude of the splitting, unaccompanied by a change in the crystal framework (in particular, without phase transitions in the lattice), is not seen in the entities customary to solid state optics. In our case the effect is present in the spectra of both probe ions, and it can be regarded as a characteristic optical property of superionic materials.

ANALYSIS AND INTERPRETATION OF THE SPECTRAL DATA

The temperature dependence of the lines in the Eu^{3+} luminescence spectra in the compound studied here, $Na_5RESi_4O_{12}$, differs in different temperature regions. At the lowest temperatures ($T < 120$–150 K) the spectral positions of the europium lines remain essentially constant. At higher temperatures, the lines begin to shift. As was shown in Ref. 6, it is at temperatures ≈ 120 K in this

material that local hops of cations across the lowest of the potential barriers begin to be seen in optical properties. The weak dependence of the positions of the lines which sets in near 120 K is of course linked with specifically the onset of a significant mobility in the cation sublattice.

At higher temperatures we see a general decrease in the amplitude of the splitting, again as has been observed[7] for the lines in the luminescence spectrum of Gd^{3+}. We interpret this dependence as reflecting a more uniform distribution of the mobile cations in the crystal lattice as the temperature is raised (Fig. 1). We understand that this process is ultimately the well-known process of defect formation stemming from the displacement of cations to interstitial positions. In the samples studied here, however, the relatively low potential barriers make this process incomparably more probable, so that consequences of this process can be observed by optical methods. This "spreading" of the charge in the lattice, like the "jellium" in Thomson's model of the atom, should evidently lead to a decrease in the fields inside the crystal and thus to a decrease in the observed splitting. In the high-temperature limit, the mobile cations, which are distributed in a fairly uniform fashion, should not contribute to the crystal field. The splitting of a multiplet under these conditions should be governed by the field generated by the O^{2-} anions of the rigid sublattice.

Formal confirmation of this fairly obvious model has been found through a repetition of the calculations from Eqs. (1)–(3) of Ref. 3 for a systematically decreasing magnitude of the effective charge of the cations. The results of these calculations are shown in Fig. 5; they are in good agreement with the experimental behavior in Figs. 3 and 4. The splitting amplitude calculated for the two multiplets decreases by some tenths as the effective charge of a cation from the second coordination sphere decreases to zero. A complete degeneracy of the levels is of course not reached, since there remains the splitting due to the octahedral field of the first coordination sphere of six oxygen anions. However, we should acknowledge that this model is so natural that a good agreement between theory and experiment should be perceived basically as proof that there are no errors in the calculations.

Finally, the most interesting and informative results in studies of the temperature dependence are the qualitative changes in the spectra, particularly, in the total number of lines in the multiplets. From the data of Ref. 3 and in Figs. 3 and 4 we can distinguish four temperature regions in which the number of lines is fixed. The numbers of lines and the boundaries of these regions are listed in Table I. (The boundaries of these temperature regions are somewhat arbitrary, for reasons which will be discussed below.) Also shown in this table is a collection of data on the spectra of the gadolinium ion.[6,8] The question mark is a reminder that the positions of all the lines of the quartet were determined for two multiplets of the three observed. The notation 4×5 (4×3) means that in this temperature region one observes a superposition of four quintets (triplets) of lines.

When presented in this form, the data reveal that the

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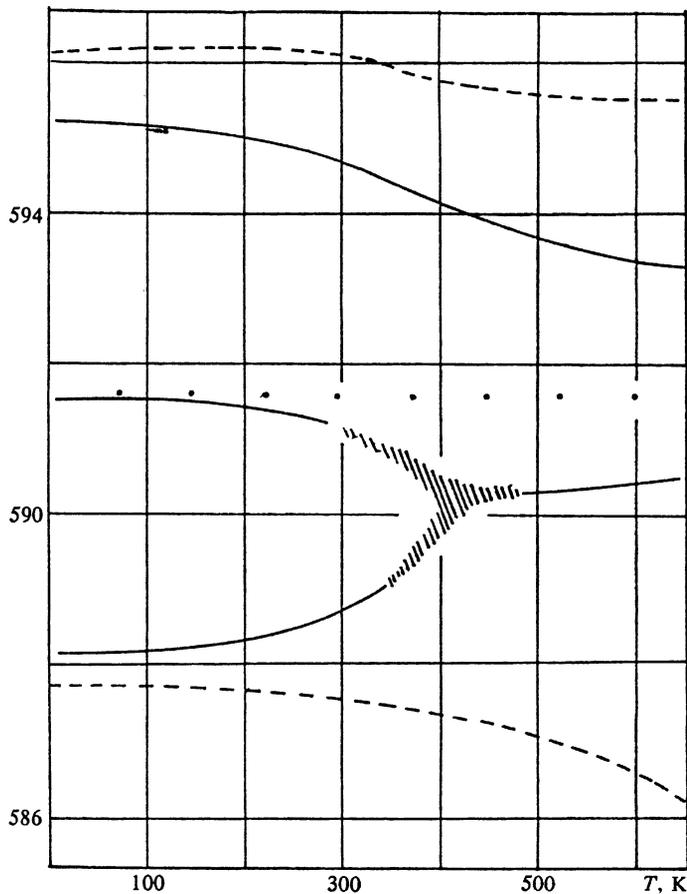
FIG. 3. Positions of lines of the $^5D_0 \rightarrow {}^7F_1$ multiplet versus the temperature. Dashed lines—Positions of the line half-heights; dotted line—positions of the center of gravity of the multiplets.

restructuring of the mobile cation subsystem which occurs with increasing temperature is a noncompound process. At low temperatures the state of the system is inhomogeneous at the microscopic level: Different states (but which are apparently close in terms of symmetry) coexist, and the spectroscopy reveals a superposition of several types of spectra. Above this temperature region (whose boundary is near 120 K), up to about 400–420 K, the difference between the various subtypes of configurations disappears because of local motions, and the RE sites in the crystal become identical. Comparison of the experimental data from Table I with the numbers of components in the multiplets for various types of symmetry which we know from symmetry considerations (Table II) reveals that below 120 K the site of the rare earth ion in $Na_5RESi_4O_{12}$ is described by a symmetry lower than tetragonal.

The number of observable lines in the spectra changes again at 400–420 K. Above this temperature region (and up to 600 K), we observe two and four lines instead of the previous triplet and quintet. According to the symmetry selection rules, this observation is unambiguous evidence of a tetragonal symmetry.

According to our interpretation, the resulting symmetry of the RE site is the result of the effects of the second and first coordination spheres. However, it is difficult to believe that the redistribution of the cations of the second coordination sphere could be predominant and could generate symmetry elements which would be absent from the first coordination sphere. As we mentioned earlier, the first

coordination sphere of the RE ion is an octahedron, distorted to some extent, of course, by the asymmetry of the surroundings. In our interpretation we assume that the resultant distortion of the symmetry of the octahedron and the effect of the second coordination sphere can single out as predominant only those symmetry elements which were originally present in the undistorted octahedron. Between 420 and 600 K the arrangement of cations thus emphasizes one of the fourfold axes of octahedra.

We should stress that, here and below, we are discussing local structural characteristics. The reason is that the region near the probe ion from which information is extracted by luminescence methods is of a local nature. However, since the sites of the RE ions are regular lattice sites, the analysis could also be conducted in terms of the symmetry elements of the crystal. We will speak in terms of local symmetry elements, since this approach is more graphic and corresponds better to the nature of the experiments which are used.

A comparison of the data in Figs. 3 and 4 reveals some important arguments pertinent to an interpretation of what happens near 420 K. In a formal analysis a change in the symmetry of a site not accompanied by a change in the rigid sublattice is a local structural transition. However, a coalescence of lines for the transition to the $^7F_1$ state occurs up to ≈ 400 K, while the coalescence of lines of the former $^7F_2$ quintet occurs at 420 K. We have already encountered a similar "disagreement" among data in an analysis of the fine structure in Ref. 3. In the case at hand the
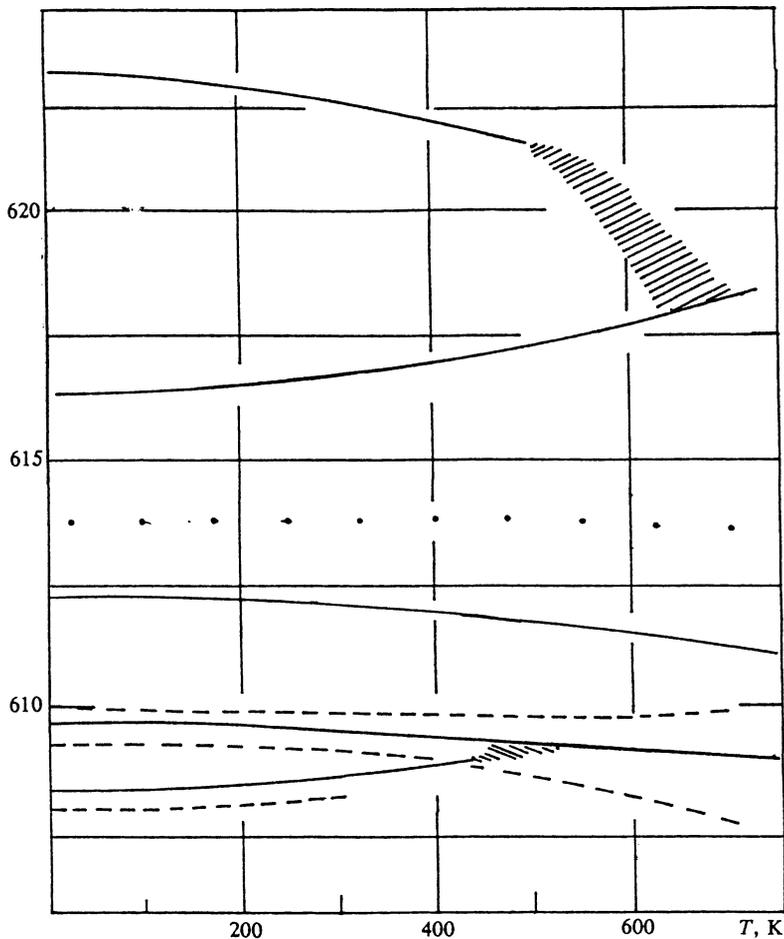
FIG. 4. Positions of lines of the $^5D_0 \to {}^7F_2$ multiplet versus the temperature. The notation is the same as in Fig. 3.

effect has the same cause: The discrepancy in terms of temperatures is again due to the very large range of sensitivity of the probe ion in the surrounding lattice. The multiplet $^5D_0 \to {}^7F_1$, after undergoing the triplet-doublet transition, probes a wider region than the $^5D_0 \to {}^7F_2$ multiplet does.[9] As a result, the transition temperature may be lowered by two independent mechanisms.

1. The large number of particles and the large number of possible configurations can be averaged out better in a region of larger volume, so the local asymmetry is averaged out earlier than it is for a region of smaller size.

2. The averaging is not only static but also dynamic (a corresponding effect was observed in Refs. 6 and 7). In this mechanism, the circumstance that the probability for the hopping of one (arbitrary) particle is larger for a large region than for a small region is important. To demonstrate this assertion, we denote by $f_0 = (E_1 - E_2)/h$ the frequency of perturbation events (in our case, hops of ions) which is required for the coalescence of levels E_1 and E_2 as a result of dynamic averaging. The probability (w) for the hopping of an individual ion contains a Boltzmann exponential function and a preexponential factor: $w = w_0 \exp(-E/kT)$, where E is the hopping activation energy. The hopping frequency averaged over the region, W, is proportional to the probability for the hopping of one of the particles. Taking the hopping probabilities of the particles to be independent, we find the following expression for the average frequency:

$$W \sim V w_0 \exp(-E/kT). \tag{1}$$

Here V is the volume of the region, which is proportional to the number of particles in it. It can be seen from (1) that, in a region of larger size, a lower temperature is sufficient to reach a certain frequency of perturbation events. For the case at hand, that result means that for the $^7F_1$ orbital the dynamic averaging should take place at relatively lower temperatures than for the $^7F_2$ orbital; this is what has been observed experimentally.

Because of the complexity of the crystal lattice, we have not been able to reliably distinguish the specific sites between which hops lead to the appearance of the necessary symmetry, as was done in Ref. 3 or Ref. 6. This circumstance, along with the superposition of mechanisms, makes attempts at numerical estimates look somewhat less than useful. Nevertheless, a comparison of the temperature regions and the difference between the frequencies of the coalescing lines for the transition near 420 K and for the dynamic averaging near 120 K (Ref. 6) unambiguously shows that the dynamic averaging near 420 K definitely must be contributing. In the second coordination sphere of the RE ion there may be an average of 4.5 Na$^+$ cations; under these conditions there is no arrangement of cations that could lead to a high symmetry by virtue of a static averaging.

Near 600 K the number of lines in the spectra changes once more. In this case the symmetry of a site becomes

cm^{-1}

1000

900

800

500

400

300

200

0   0,2   0,4   0,6   0,9 $1 - q/q_0$
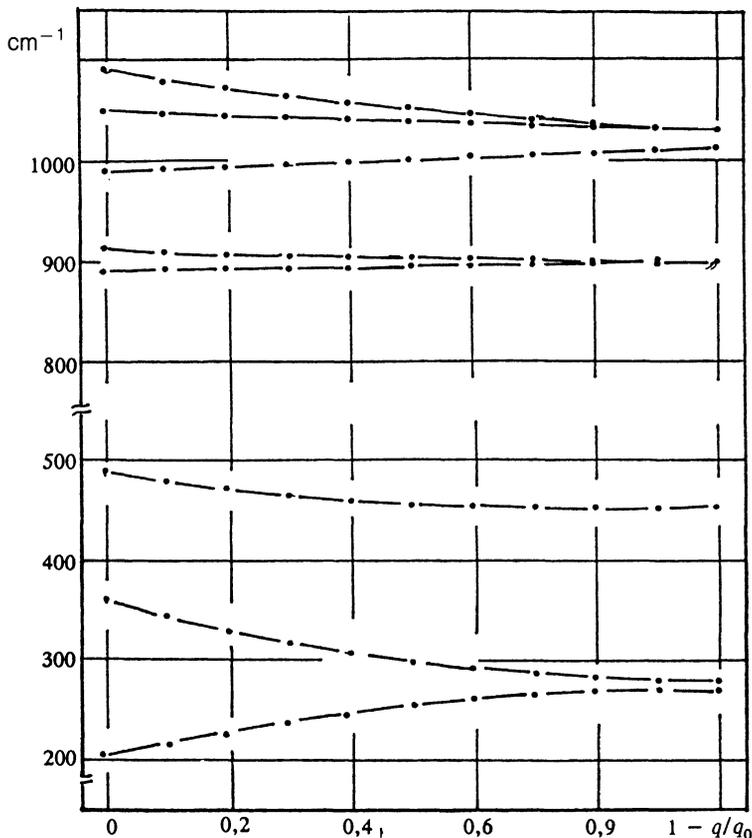
FIG. 5. Positions of the lines of the multiplets $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_2$ versus the effective charge of the Na^+ cation from the second coordination sphere of the Eu^{3+} ion (calculated).

hexagonal. The original symmetry group of the octahedron contains the element $S6$, which becomes predominant as a result of the summation of contributions of the perturbations. It has not been found possible to find a static combination of stable types of configurations near the RE site which would lead to the corresponding symmetry. On the other hand, the number of observed lines is unambiguous evidence that the symmetry of the site is fairly high (probably only $S6$). The contradiction which has arisen here can also be resolved in the model of a dynamic averaging, in which any configuration of cations can change to the inverse configuration over the lifetime of the excited state of the probe ion, so that the asymmetric components of the crystal field can be effectively averaged out.

The transition to a highly conducting state in the superionic material $Na_5RESi_4O_{12}$ is therefore a cascade of local structural transitions with local changes in symmetry. It can be asserted quite confidently that each of these structural transitions is a local dynamic averaging of cation configurations, in regions of progressively increasing size. In principle, this concept finds indirect confirmation in the results of Ref. 10, where a partial restructuring of a mobile cation subsystem was detected near 150 °C. According to Ref. 10, the difference between the populations of two groups of four close-lying sites, Na_5, 6, 6', and 5', disappeared. This result agrees well with the concept of a dynamic averaging. However, the method used in Ref. 10, particularly the long averaging time in the experiments, prevents us from accepting the data found there as direct evidence in favor of the model of a dynamic nature of the changes in the mobile sublattice.

We pointed out in Ref. 7 that a similar structural transition could have certain distinctive features from the thermodynamic standpoint. Let us go into that question in more detail. Formally, a change in the number of lines in a spectrum means a change in the symmetry of the lattice site. Since the RE sites are regular lattice sites, this change is equivalent to the existence of a structural transition of the entire crystal lattice. The positions of the lines do not change abruptly near the coalescence temperatures of 420 and 600 K, for either the $^7F_1$ multiplet or the $^7F_2$ multiplet. According to the Landau criterion, a structural transition of this sort, in which the material in the low-temperature neighborhood of the transition point is indistinguishable

TABLE I.

Levels	Numbers of lines			
	Below 120 K	120 — 420 K	420 — 600 K	Above 600 K
$^7F_1$	4×3	3	2	2
$^7F_2$	4×5	5	4	3
$^6P_{7/2}$ (Gd^{3+})	3×4 (?)	4	4	4

TABLE II.

Symmetry	Number of components for the levels of			
	europium			gadolinium
	$^7F_0$	$^7F_1$	$^7F_2$	$^6P_{7/2}$
Cubic	1	1	2	3
Hexagonal	1	2	3	4
Tetragonal	1	2	4	4
Lower	1	3	5	4

from the high-temperature form, is a second-order phase transition.[11] In our case, however, the transition is quite different from the typical symmetry-changing structural transitions which second-order transitions are. In $Na_5RESi_4O_{12}$, because of the small number of cations in the coordination sphere of the probe ion, steady-state configurations with a high symmetry could not arise at all. A high-symmetry state could therefore arise only as the result of the disappearance (on the average) of asymmetric components of the crystal field upon an averaging between alternating types of configurations which are mutually inverse with respect to the central probe ion.

A transition to a high-symmetry state is not merely a transition to a new structure but also—and to the same extent—a transition to new types of motion. We suggested the term "dynamic structural transition" for such transitions in Ref. 7. Structural transitions of this sort, involving a change in symmetry due to a change in the state of motion, have yet to be taken up theoretically, to the best of our knowledge. We understand on the basis of general considerations that a transition to new states of motion may require energy to complete the transition, as in ordinary melting. Although we have not been able to experimentally observe evidence of a latent heat of transition near 400–420 K, the reason may be that in our case the restructuring involves a relatively small part of the crystal lattice. We regard the question discussed in this section of the paper as extremely important, since phase transitions which are something between first-order and second-order are encountered fairly frequently in superionic conductors.

In principle, one could find another point of view, according to which this concept regarding the nature of the local changes in symmetry which occur as a dynamic averaging of cation configurations would look completely natural. For this purpose we compare the situation which prevails in a superionic conductor with that in an ordinary liquid. In each case, heavy particles with a mass on the order of 10^4–10^5 times the electron mass are mobile, and the de Broglie uncertainty in the coordinates of the particles is fairly small. Consequently, a high symmetry cannot be achieved as the result of the quantum-mechanical uncertainty in the positions of the particles. In both cases, there are random configurations around the probe ions at each instant of time; in general, these random configurations are by no means symmetric. On the other hand, at sufficiently high temperatures the spectrum corresponds to a high symmetry in both cases. The case of an ion in a liquid is a classic example which can be clearly understood as the result of a dynamic averaging. The case of a super-

rionic conductor which we have looked at is similar in nature to a charged liquid in a crystal lattice, so this concept regarding the nature of the observed series of transitions looks correct.

CONCLUSION

Various experiments have been carried out by methods of probe-ion optical spectroscopy in order to learn about the mobile cation subsystem of a superionic material belonging to the "nasicon" family: $Na_5RESi_4O_{12}$. The ions used for this study were the Eu^{3+} ions. The data found agree well with results found previously with the help of Gd^{3+} probe ions.

In the course of the study we observed numerous effects which add substantially to existing ideas regarding the processes which occur in the mobile sublattice of superionic materials. In particular, in the first study of this series,[3] it was shown by optical methods that there is a latent structural note in the sublattice of mobile cations, which has traditionally been regarded as disordered. The types of stable cation configurations were determined. The positions of spectral lines for RE ions in these configurations were calculated. The results of these calculations turned out to agree well with experimental data. We also determined certain low-probability configurations, which apparently serve as intermediate stages for ion transport processes.

The absence of a general phase transition to a highly conducting state in crystals of this family has made it possible to trace the process by which a conducting state arises gradually as the temperature is raised. Optical methods have made it possible to observe effects stemming from a displacement of ions to interstitial positions and effects stemming from a dynamic averaging. On the whole, the results make it possible to picture the process by which a superionic state is reached as a cascade of local structural transitions in which a dynamic averaging of cation configurations is carried out successively in regions of different sizes.

Note also that effects which arise with increasing temperature are important not only in themselves but also because they constitute new physical phenomena similar to a dynamic structural transition. In principle, the structural units observed in Ref. 3 could also be of a different nature, unrelated to a superionic conductivity: They might reflect the presence of twinning regions or regions of other structural defects which are typical of the given material. How-

ever, it is the nontrivial change in the spectra with the temperature—a change which is evidence of a radical but still reversible change in structure with the temperature—which ultimately proves the validity of this interpretation.

This has been the first such systematic study of a mobile cation subsystem by luminescence methods. Most of the results are qualitatively new. In general, it is fair to say that this study demonstrates the benefit of using luminescence methods to study superionic conductors.

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