Eu^{3+} ion-probe spectroscopy in the superionic conductor $Na_5YSi_4O_{12}$ at low temperatures: investigation of the structure of the disordered sublattice

M. E. Kompan and G. B. Venus

A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences

(Submitted 20 May 1992)
Zh. Eksp. Teor. Fiz. **102**, 1424–1432 (October 1992)

The properties of Eu^{3+} ions in the lattice of the superionic conductor $Na_5YSi_4O_{12}$ are studied by selective laser spectroscopy methods. Experimental data are used to analyze the properties of the mobile Na^+ sublattice. The existence of stable multiparticle configurations in the "disordered" sublattice of mobile ions is demonstrated; the specific types of ion arrangements are reconstructed, and their relative probability is determined.

INTRODUCTION

The present level of understanding of the rules governing the structure of a sublattice of mobile cations, and of the mechanisms governing the high ionic conductivity of superionic conductors, is clearly inadequate; it does not permit formulation of anything like an adequate picture of such phenomena as superionic conductivity. This is partly due to the limitations of the traditional set of experimental methods for studying these materials. By nature superionic conductors are simultaneously disordered and dynamic materials. This limits the possibility of diffraction methods, which are predicated on averaging over many lattice periods and, simultaneously, over the exposure time. Optical methods, in particular the methods of contemporary laser spectroscopy, do not have these shortcomings, and allow one to obtain information about local regions of the disordered structure while investigating the kinetic characteristics.

Attempts have been made in several other studies, for example those of Refs. 1 and 2, to apply optical ion-probe spectroscopy to superionic conductors; however, as a rule, the authors limited themselves to determining the anomalies in separate properties, and no concrete data on the structure of the mobile sublattice was obtained in the studies familiar to us.

The investigations described here are an application of the methods and approaches of optical spectroscopy to the study of a set of problems connected with the melted sublattice in materials of the family $Na_5RESi_4O_{12}$ (where RE represents a rare-earth element). We have previously carried out a series of studies on spectroscopy of the Gd^{3+} ion in this same material; these allowed us to obtain, by optical methods, qualitatively new information on the composition of the mobile sublattice of a superionic conductor (see references in the review article of Ref. 3). As is well known,[4] the properties of the Eu^{3+} ion are substantially different from those of Gd^{3+}, and results obtained using these ion probes do not duplicate each other. Thus we can get much more detailed information in this study.

OBJECTIVE

At present $Na_5RESi_4O_{12}$, among other materials structurally similar to the so-called Nasicon,[5] is under consideration as a prospective material for various applications in power engineering.[6] Until recently, relatively few fundamental studies had been carried out in this connection. However, the results obtained in our work show that due to certain features of the structure, this material can be considered a model compound, the study of which is very informative.

The properties of superionics of the $Na_5RESi_4O_{12}$ family have been repeatedly discussed in our previous publications.[3] Here we will only point out that these materials are conducting in the Na^+ cation, with an activation energy of 0.21–0.23 eV (depending on the type of RE ion). Sodium diffusion proceeds along channels about 3.5 ± 0.2 Å from the RE ions, which occupy regular positions in the lattice. The sites forming the diffusion channels also make up the second coordination sphere of these ions; the first coordination sphere of the RE ions is made up of a rather regular oxygen octahedron $6O^{2-}$. A lattice site with a RE ion and its neighbors in two first coordination spheres is shown, somewhat schematically, in Fig. 1.

The possibility of studying the mobile sublattice via the RE^{3+} ion luminescence is related to the fact that the positions in the diffusion channel are probabilistically occupied, and the distribution of mobile cations, and their hops, are expressed in the crystal field at the RE^{3+} site, and correspondingly in the level splittings and line positions.

We use the experimental technique and methods described in our studies of Gd^{3+} spectroscopy.[3]

EXPERIMENTAL RESULTS

The Eu^{3+} ion luminesces in the visible, in the red region of the spectrum. The general appearance of the spectrum

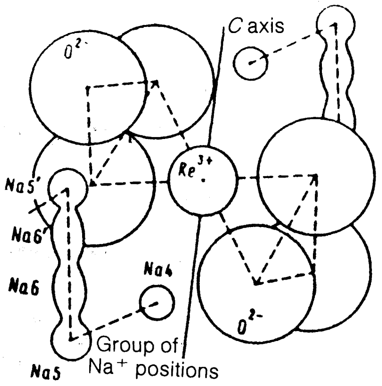

FIG. 1. Schematic arrangement of a lattice fragment in $Na_5RESi_4O_{12}$, containing ions of the first and second coordination spheres around the RE ion. The oxygen anions of the octrahedron of the first coordination sphere are separated in the drawing to show the central ion and to emphasize the hexagonal symmetry of the high-temperature phase.

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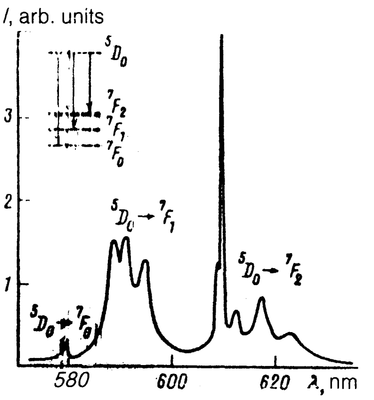

FIG. 2. A general view of the luminescence spectrum of the Eu^{3+} ion in $Na_5RESi_4O_{12}$ at room temperature and the cooresponding level spectrum. Under the given conditions, the $^7F_1$ level is split into three sublevels, and $^7F_2$ into five sublevels.

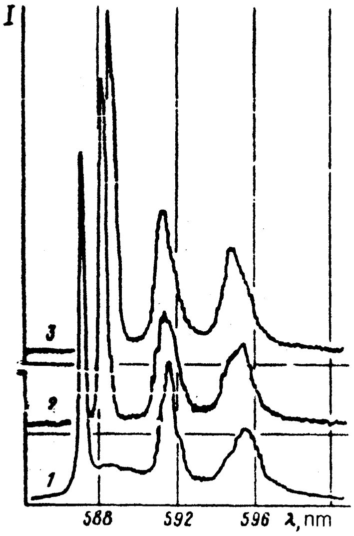

FIG. 3. Luminescence spectrum for the transition $^5D_0\rightarrow{}^7F_1$ for several values of λ_{exc} ($T = 4.2$ K): *1*—$\lambda_{exc} = 5789.8 \pm 0.15$ Å; *2*—5795.0 ± 0.15 Å; *3*—5800.2 ± 0.15 Å.

when it is excited by photons of energy 4 eV, and a level drawing, are shown in Fig. 2. It is seen that under such excitation conditions the spectral lines are rather broad, as they should be in materials with disorder; groups of lines corresponding to different multiplets do not overlap in the spectrum.

To reveal the hidden structure in the nonuniformly broadened lines of our spectrum, we use, as in Ref. 7, a study of the luminescence spectra for different excitation wavelengths. Because splitting of the ^7F_J Eu^{3+} ion levels is shown by the final levels of the luminescence transitions, low lattice temperatures in this case do not cause "freezing out" of lines in the spectrum. Therefore, the isolation of separate multiplets for the case of (Eu^{3+}) turns out to be much simpler than for Gd^{3+}. In the experiments, luminescence was excited in the transition region 579–580 nm ($^7F_0\rightarrow{}^5D_0$), so that the spectral regions of luminescence and excitation were separated. Several typical spectra for the $^5D_0\rightarrow{}^7F_1$ transition, for different wavelengths λ_{exc} of excitation illumination, are shown in Fig. 3. The data cited in the figure demonstrate that the magnitudes of the line shifts are so large that they can be accurately distinguished from the background of the line width.

Since in the present case the position of the luminescence line and the position of the excitation line are simultaneously changing, the luminescence spectrum alone or the excitation spectrum alone does not convey much information. In Fig. 4 cumulative data are presented in a two-dimensional representation—the dependence of the position of the luminescence line on λ_{exc} for the triplet $^5D_0\rightarrow{}^5F_1$ and the quintet $^5D_0\rightarrow{}^7F_2$. In the lower part of the figures, along the abscissa, the shape of the nonuniformly broadened line $^7F_0\rightarrow{}^5D_0$ at the excitation wavelength is shown for scale.

Figure 4 shows the variation in line position as a function of the wavelength of light exciting the luminescence. We

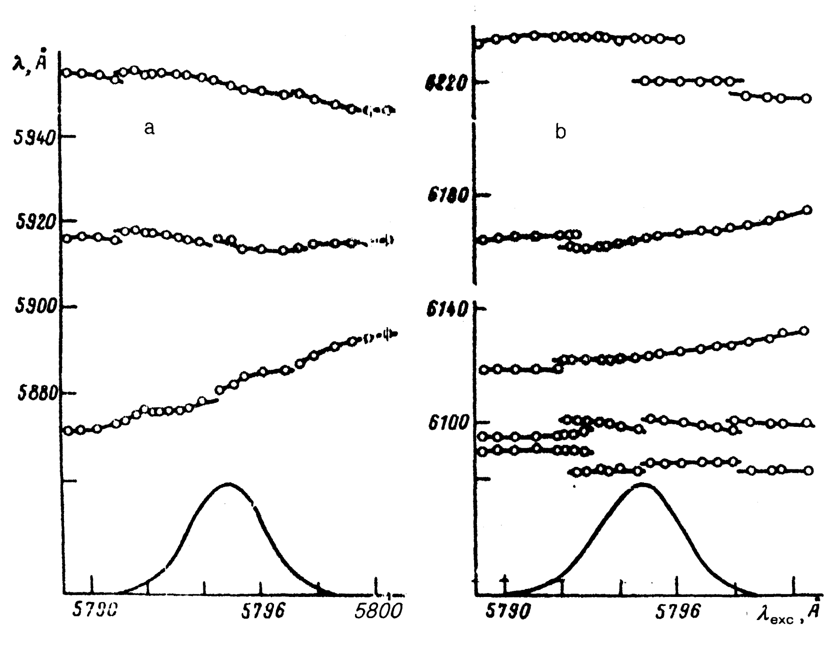

FIG. 4. Dependence of the luminescence line positions on the excitation wavelength for the triplets $^5D_0\rightarrow{}^7F_1$ (a) and $^5D_0\rightarrow{}^7F_2$ (b). The excitation is in the region of the transition $^7F_0\rightarrow{}^5D_0$; in the lower part of the figure the profile of the inhomogeneously broadened line for this transition is shown for scale ($T = 4.2$ K).

also note that the curves are not monotonic; they show distinct gaps and discontinuities, and in some intervals of excitation wavelength there are regions in which the fine structure of two multiplets coexists, so that the total number of lines exceeds the maximum allowed for a given multiplet.

The fact that the line position varies with λ_{exc} is not in itself remarkable; it indicates that ions can be selectively excited with a certain type of environment out of the rather wide variety created by disorder. In our case it is important that the dependence obtatined is not continuous. The lack of continuity in this case has approximately the same meaning as the discrete nature of optical spectra of atoms. In atoms discreteness signifies that only certain states with certain energies are allowed, and the intermediate states are forbidden. In our case the reason for the splitting is the perturbation of the crystal field by the surrounding cations; the lack of continuity in the dependence signifies the absence of a continuous set of coordinating distributions. The data for both multiplets show that there are four regions of excitation wavelength in which the spectral dependences are continuous, but between which there is no continuous transition. This signifies the existence of four basic types of particle configurations in the RE-probe environment. The existence of continuous intervals in the spectral dependence signifies that the stable configurations tolerate some diffusion, but the basic fact that there are no intermediate configurations remains.

The experiments on Eu^{3+} confirm the conclusion reached on the basis of study of Gd^{3+}—that in the melted cationic sublattice there are only a small number of stable types of cation configurations.[7] In comparing the results we especially note that in the case of europium there are four, and not three (as for gadolinium) separate multiplets. This does not lead to any serious contradictions between the data obtained, as the additional fourth multiplet in Eu^{3+} is weak and mixed, for short wavelengths, with a relatively dominant pair of intense multiplets. In the spectrum of the Gd^{3+} ion such a multiplet would be overlapped by other lines of the quartet, and observation would be difficult.

ANALYSIS AND DATA INTERPRETATION FOR THE SPECTRAL EXPERIMENT

1. Intense multiplets

An analysis of the possible types of stable cation configurations was carried out in Ref. 7. This analysis was based on qualitative general physical considerations which none the less allowed determination of the specific types of configurations. All the discussions and arguments there are also applicable in the present case. As was already explained, the experimental data for Eu^{3+} and Gd^{3+} are also in agreement. However, the existence, for the Eu^{3+} ion, of rather well developed calculational methods already described in the literature (see, for example, Ref. 8) opens additional possibilities.

An attempt has been made to confirm by calculation the accuracy of the types of configurations found on the basis of qualitative considerations. The equivalent operator method was used.[8] In this way we can find the magnitude of the level shifts resulting from the perturbing action of the crystal field on the ion levels $^7F_0$, $^7F_1$, and $^7F_2$.

In this case the Hamiltonian for states with total momentum J can be written in the form

$$H_{\text{cryst}} = \sum_{n=2,4,6} \theta_n \sum_{m=-n}^{m=n} B_n{}^m \hat{O}_n{}^m. \tag{1}$$

In this expression $\hat{O}_n^m$ are the equivalent operations, B_n^m are the crystal-field parameters, and θ_n are the Stevens coefficients.[9] The matrix element of the state $^{2S+1}L_J$ with projection J_z is given by the expression

$$\langle SLJJ_z | H_{\text{cryst}} | SLJJ_z{}' \rangle = \sum_n \frac{1}{2^n} \left[\frac{(2J+n+1)!}{(2J-n)!} \right]^{1/2} \times \theta_n \sum_m \begin{pmatrix} J & n & J \\ -J_z & m & J_z{}' \end{pmatrix} (-1)^{J-J_z} B_n{}^m. \tag{2}$$

Here the factor in the form of a 2×3 matrix is the Wigner symbol.[10]

In our case, since the energy gap between the three lowest ^7F_J levels is comparable with the crystal splitting of the levels, the level perturbation must be studied concurrently. The expression for the matrix element $\langle SLJJ_z | H_{\text{cryst}} | SLJ'J'_z \rangle$ is also known and is cited in Ref. 8. Thus, for known values of the parameters B_n^m, having calculated the eigenvalues of the ninth-order matrix, we can evaluate the positions of the Stark constants of the Eu^{3+} ion.

Various models for calculating the parameters B_n^m are known. We will use the most common, and simplest, model of point charges.[11] In this approximation the crystal field parameters are calculated according to the known positions of the surrounding ions from the formula

$$B_n{}^m = \rho_n A_n{}^m = \rho_n \frac{4\pi e^2}{(2n+1)} \sum_j \frac{q_j}{R_j^{n+1}} Y_{nm}^{*}. \tag{3}$$

Here ρ_n is a constant proportional to the average value of the nth power of the screening radius, characterizing the screening of the $4f$ shell (tabulated in Ref. 12); the A_n^m are ion-independent constants B_n^m; R_j is the radius vector of the corresponding ion, and the Y_{nm}^* are the spherical harmonics.

The calculation according to equation (3) was carried out by taking account only of the ions in two coordination spheres—the oxygen ligands and the second coordination sphere, including the positions of the mobile Na^+ cations. The results of this calculation and their comparison with experimental values are presented in Table I. It is evident that, the approximate nature of the calculation notwithstanding, completely satifactory agreement is obtained between the calculated positions of the energy levels and those actually observed.

These same results, obtained for the Eu^{3+} ion-probe, agree with experimental results for Gd^{3+}, and open up the possibility of a calculational confirmation of the types of cationic configurations found by qualitative considerations.

2. Weak multiplets

As noted above, the europium-ion luminescence spectrum is a superposition of two intense and two weak multiplets. To explain the configuration types corresponding to the weak multiplets, we take into consideration that they must, as far as possible, satisfy the criteria chosen earlier: optimal approximation to electroneutrality, optimal approximation to the statistically average occupation numbers

TABLE I.

Level	Sublevel position, cm^{-1}		Baricenter position, cm^{-1}		(relative to $^7F_0$ level)
	Experiment	Calculation	Experiment	Calculation	
First intense multiplet					
$^7F_1$	244	207	359	356	Configuration RNa5Na5′ – GNa4Na6
	363	361			
	470	497			
$^7F_2$	823	892	977	985	
	869	908			
	928	990			
	1032	1050			
	1225	1086			
Second intense multiplet					
$^7F_1$	261	224	352	342	Configuration RNa5Na5′ – GNa4Na6′
	344	352			
	449	451			
$^7F_2$	823	889	964	964	
	858	903			
	925	972			
	1035	1002			
	1176	1053			
Level difference between the two fundamental multiplets, cm^{-1}					
$^7F_1$	−17	−17	7	14	
	19	9			
	21	46			
$^7F_2$	2	3	13	21	
	11	5			
	3	18			
	−3	48			
	49	33			

for different ion positions; minimal Coulomb repulsion energy.

Configurations of the type A in Fig. 5 in fact satisfy the requirements cited; however, the total charge of each such configuration is $+4e$, while the average charge should be near $+3.6e$ (from which, by the way, it follows that it is not possible to fill the crystal with any single configuration).

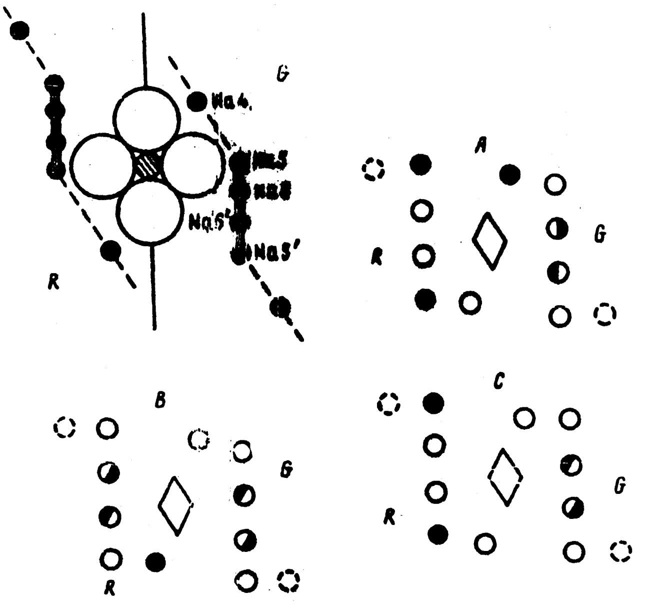

FIG. 5. Distribution of the conduction channels in the neighborhood of the RE ion and positions of the Na^+ cations: R, G are channel indices; A, B, and C are the three most probable groups of cation configurations. Within the groups different configurations are possible, due to occupation of one of the two nearby positions Na6 or Na6′ (the half-filled circles); filled circles are positions taken by the mobile sodium cations; open circles are unoccupied positions. The dashed circles are the positions of the sodium ion in the conduction channel, at the boundary of the second coordination sphere of the ion-probe; the rhombus gives the orientation of the ion-probe relative to the ionic conductivity channel.

This leads to consideration of the probability of appearance of three-cation configurations around RE ions. A general analysis of three-cation configurations allows us to identify the most probable configurations (types B and C) as those drawn in Fig. 5. Each of the configurations shown is a group of close types, which can differ within a group by the transfer of a cation between positions Na6 and Na6′ and the inversion of population between channels.

The relative probability of each of the configurations ($w_j : j = A, B, C$) can be determined from the normalization condition

$$\sum w_j = 1 \tag{4}$$

and the condition for obtaining reliable statistically-averaged populations n_i for each position, in accordance with the known x-ray data:[13]

$$\sum_j w_j \frac{N_{ij}}{M_i} = n_i. \tag{5}$$

Here N_{ij} is the number of occupied positions of the type i in the configuration j; M_i is the number of i-type positions in the coordination sphere. Conditions (4) and (5) are redundant, but they allow us to find the set of values $w_A = 0.64$, $w_B = 0.27$, and $w_C = 0.08$, satisfying the equalities cited above to an accuracy of 0.01. Attempts to use additional types of configurations in the calculations only caused conditions (4) and (5) to be satisfied less well. Thus we may say that the new types of ionic configurations found here, like the first ones, correspond to the physical situation.

A calculation of the multiplet levels in accordance with configurations B and C has not been carried out. However, considering the difference in the values of w_B and w_C, it is not probable that the observed weak multiplets correspond to configurations B and C. It appears that they may arise as a manifestation of the inequivalence of the configurations within the basic group B.

DISCUSSION OF THE RESULTS

Thus, spectral investigations of the Eu^{3+} ion states in the superionic conductor $Na_5RESi_4O_{12}$ have proven to be a sensitive and informative way of studying the melted sublattice. The fundamental result of the investigations—the discovery and identification of the stable cationic configurations in the mobile sublattice—reliably confirms the conclusions reached in Ref. 7, on the basis of qualitative considerations, about the specific types of configurations.

It is important to discuss in more detail several of the results obtained. In particular, a close inspection of the data of Figs. 3 and 4a reveals that the anomalies in the spectral dependence (gaps, etc.) are substantially more pronounced for the $^5D_0 \rightarrow {}^7F_2$ transition than for the $^5D_0 \rightarrow {}^7F_1$ transition. Since both groups of lines pertain to the same ions in the same crystal, under identical conditions, this fact is nontrivial. The explanation lies in taking account of the differences in the dependence of the crystal-field constants on the radii of the surrounding ions. This problem was pursued in detail in Ref. 12, where it was shown that the crystal-field constants B_2 determining the splitting of the $^7F_1$ multiplet effectively depend on the distribution of neighbors in a sphere of radius up to 15 Å; the B_4-type constants for higher crystal-field harmonics, which begin to enter into the expression for the $^7F_2$ multiplet splitting, effectively contain a contribution from a much smaller neighborhood of the RE ion—a radius of about 5 Å. A radius of order 5 Å, in our case, just marks the boundary between the second and third coordination spheres of the ion-probes. In principle both the second and third coordination spheres consist of positions randomly populated by mobile cations. But if the second coordination sphere contains ten positions with an average total occupation of about 3.6 ions, then the next coordination sphere contains an order of magnitude more ions and positions. Therefore the set of discrete cationic configurations occuring in a region of small dimensions, when considered together with a region of substantially larger radius, turns into a quasicontinuous set of possible variations of distributions, which "smears out" the initial discreteness.

We also emphasize that the transition between examining a region of one extent and examining a different region has not been determined in this case by the subjective wishes of the experimenter, but is connected with the properties of the ion-probe itself. This opens up the possibility, in principle, of a "layered" probe of the crystal around the ion, and also underscores the relativity of the concepts of discreteness and continuity in our case.

We also point out that for a relatively crude approximation in calculating the line positions yields rather good agreement with the experimental data. We relate this to the fact that the materials studied are close in chemical composition to a traditional object of spectroscopy—silicon glasses with Re^{3+} ions—and use of calculational methods and known empirical constants developed for glasses is adequate in our case.

A problem of particular interest is the correspondence of the predicted cationic configurations we have found to the state of a superionic conductor at higher temperatures, where its conductivity typically reaches values of 0.1–1 S/cm. Since our data relate to the spectroscopy of narrow lines, we cannot answer this question experimentally. Nonetheless, by taking account of the very small variation in population of positions with temperature,[13] and of the fact that the energy of interionic correlation is on the order of a fraction of an electron volt, we can say that the configurations we have found exist and determine the organization of the mobile sublattice at higher temperatures as well.

The authors thank A. K. Przhevusskiĭ and M. N. Ponovaya for discussions of the materials of this study.

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Translated by I. A. Howard