

Dynamic averaging of stable cation configurations in the superionic conductor $\text{Na}_5\text{RESi}_4\text{O}_{12}$

M. E. Kompan, G. B. Venus, and O. V. Dimitrova

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

(Submitted 10 August 1990; resubmitted 31 October 1990)

Pis'ma Zh. Eksp. Teor. Fiz. **52**, No. 11, 1185–1189 (10 December 1990)

A dynamic averaging of stable configurations of Na^+ conduction cations in a superionic conductor has been observed by optical spectroscopy for the first time. The experimental results are interpreted as confirmation that the model of a two-level system can be applied to superionic conductors.

Superionic conductors are attracting research interest because of their unique and effective technical applications and also because of the variety of properties which reflect their dual nature: something between a liquid and a solid.¹ Essentially any classical objects or ideas from the physics of the condensed state may have close analogs or direct applications in some phenomenon involving superionic conductivity. In some cases these analogies might point out some promising directions for research.

An attempt was made in Ref. 2 to use the model of a two-level system to analyze the properties of a superionic conductor. That approach looks promising, since the concept of a two-level system is fairly versatile, so general results established for two-level systems could also be used to analyze processes in superionic conductors. The starting point for the approach developed in Ref. 2 was the suggestion that it might be possible to identify local structures (clusters or typical configurations of mobile ions) which could be in either of two possible states.

In the present study we have selected a specific superionic material: single crystals of $\text{Na}_5\text{RESi}_4\text{O}_{12}$ (where RE is a trivalent rare-earth element). By optical spectroscopy, we have succeeded in demonstrating the validity of the picture of a two-level system as the elementary structural unit of a superionic conductor. As part of this study, we have observed—for the first time in materials of this class—a dynamic averaging of various types of cation configurations of a mobile sublattice.

We studied the luminescence of rare-earth ions, Gd^{3+} , in the general chemical formula of the compound. In these crystals the rare-earth ions assume regular positions in the crystal lattice: at the centers of regular octahedra of six oxygen (O^{2-}) ligands. The Na^+ conduction cations occupy positions in “diffusion channels” in a probabilistic fashion. These channels are arranged in an asymmetric fashion near an octahedron. As a result, the symmetry of the rare-earth ions is reduced to C1, the positions of the sublevels of the emitting states are shifted, and these ions become effective probes for studying the sublattice of mobile cations.

It can be concluded from the results of Ref. 3 on the spectroscopy of Gd^{3+} ions in these materials that at low temperatures there are predominantly only two local configurations of cations among allowed positions, in contrast with the widespread

opinion that there is a complete disordering of the sublattice of conduction cations. The arrangement of cations is shown in slightly simplified form in Fig. 1. The difference between the two configurations, which are close in probability, lies in the position of one of the cations, which can occupy either the so-called Na6 position or its equivalent neighbor Na6', which lies 0.85 Å away from the first position and is separated from it by a potential barrier on the order of 10 meV. The height of this barrier has been estimated in the single-particle approximation from experimental data on the average density of Na⁺ cations.⁷

Analysis of the spectral data thus indicates that the local cation configuration might be discussed as a two-level system. Note that two, coupled, two-level systems are thus manifested in the object of interest: a first, ionic two-level system, which is directly associated with the sublattice of mobile ions and the superionic-conductivity processes, and a second two-level system, which is the subsystem of electron levels of the 4*f* shell of the Gd³⁺ probe ions. In the latter subsystem, optical transitions are observed only between the lower ⁶P_{7/2} sublevel and the ⁸S_{7/2} ground state under the conditions of low-temperature experiments. States of the electron subsystem are detected directly in the experiments; these states are in turn determined by the nature of the cation surroundings of the Gd³⁺ ions, i.e., by the state of the ion subsystem.

A similar situation has been discussed in several previous studies,^{4,5} and we will draw on results of those studies in interpreting the results of our observations. In particular, a characteristic property of these systems is a dynamic averaging: An increase in temperature causes the lifetime of the configuration of cations in a certain state to become shorter than the lifetime of the electron subsystem in the excited state. In the case at hand—the luminescing Gd³⁺ ion in an ionic conductor—the meaning is that the frequency at which the Na⁺ conduction cation hops between neighboring positions becomes higher than the difference between the frequencies of the observable components of a fine-structure doublet. This dynamic averaging should be observed, regardless of the nature of the particular two-level system. An observation of this

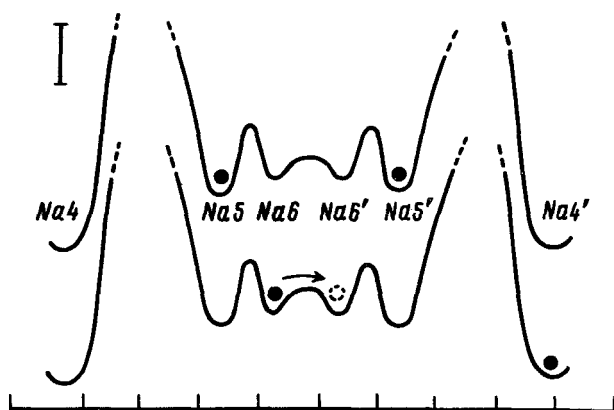


FIG. 1. Schematic diagram of cation configurations which are realized in the second coordination sphere of the luminescing Gd³⁺ probe ion. The horizontal scale division is 1 Å; the vertical bar corresponds to 10 meV.

averaging would thus confirm the validity of the model of a two-level system in our case.

We accordingly studied the temperature dependence of the positions of the fine-structure components. The wavelength of the tunable laser used to excite the luminescence was chosen in such a way that the two components, corresponding to the two basic types of cationic configurations, would be excited with equal efficiencies. Luminescence spectra were studied in the case of a nonselective excitation in Ref. 6.

The results are shown in Fig. 2. It can be seen from this figure that at low temperatures the long-wave line of the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ quartet is a doublet and that this structural feature persists to 120–125 K. At higher temperatures, only a single line is observed in the spectrum. Shown in the same figure are the positions and half-widths of the lines. Since there are other lines of a multiplet on the short-wave side of the doublet, the half-width can be determined more reliably from the long-wave edge. It can be seen from these results that the width of the line changes only insignificantly in the process. This result supports the assertion that the observed coalescence of lines is not due to a trivial effect (a broadening of the fine-structure components) and is indeed due to a decrease in the separation between these lines. A tendency toward this

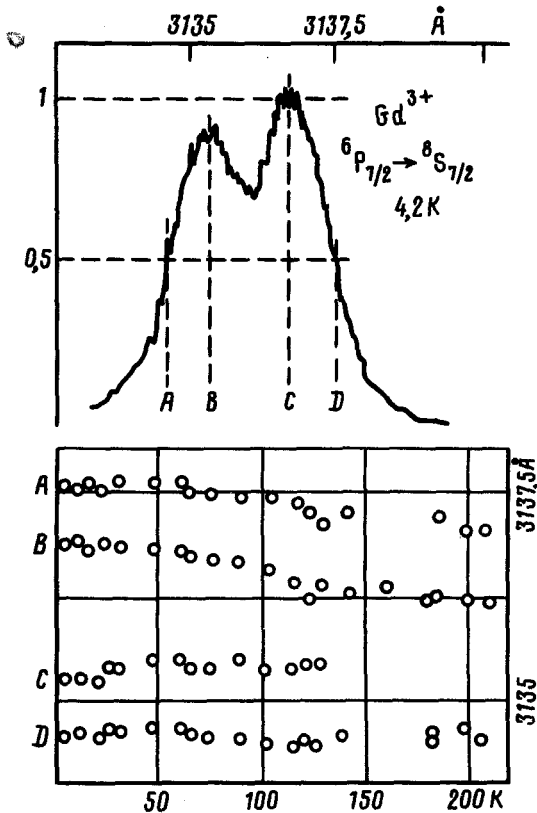


FIG. 2. Doublet structure and temperature dependence of the positions of the components of the fine structure of the long-wave line of the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ quartet.

effect can be seen clearly on the long-wave component of the doublet in the region 70–120 K.

Let us estimate the temperature at which the doublet collapses according to the model of a dynamic averaging of a coupled pair of two-level systems. In accordance with this model, we would compare the kinetics of the ion subsystem with the lifetime of the excited state of the probe ion (an analog of T_2 in MNR or ESR). However, direct measurements of the decay time of the emission intensity provide information about a different characteristic: the lifetime of the ensemble (an analog of T_1) of excited states. It can be shown, however, that the frequency difference between the components of the fine structure can be used as a temporal criterion which is close to the lifetime of the excited state.

The components of a doublet differ if, over the lifetime of the configuration of the surroundings, the corresponding oscillators emit trains of different numbers of oscillations, i.e., $|N_1 - N_2| > 1$. The number of oscillations in an emission train can easily be expressed in terms of the oscillator lifetime T_l and the corresponding oscillator frequencies f_1 and f_2 . As a result, the inequality written above becomes

$$1/T_l > |f_1 - f_2|.$$

This result shows that relationship between the lifetime of the excited state and the frequency difference between the components for which the doublet will be observed separately.

At low temperatures the frequency difference between the components of the fine-structure doublet is about 5×10^{11} Hz. To estimate the frequency of hops of ions between neighboring minima Na6 and Na6', we use the Arrhenius equation $\nu = \nu_0 \exp[-E_{\text{act}}/(kT)]$. The frequency ν_0 of the "trial" oscillations of the Na^+ cations for the Na4 position was estimated in Ref. 7 on the basis of the data of Ref. 8 on the spatial density of conduction cations. The values of the curvature of the potential function at the potential minima Na4 and Na6 are approximately the same, so we can use the value $\nu = 6 \times 10^{11}$ Hz from Ref. 7. (Actually, the value 6×10^{12} Hz is printed in Ref. 7, but that is an error). It follows immediately that the components of the doublet should be observed separately at temperatures below the energy of the activation barrier, i.e., below about 120 K.

Unfortunately, such a good agreement between the observed and calculated values is probably just fortuitous. In the first place, the "rigid" sublattice in superionic conductors also varies with the temperature. The change in the potential profile for the motion of the sodium cations is ignored in our estimates. It seems quite likely, by the way, that this circumstance is the reason for the abrupt coalescence of the doublet components (i.e., in a narrow temperature interval). We have also ignored effects of a polaron nature, which should result in an increase in the activation energy. This circumstance also provides some justification for using the Arrhenius equation with $kT \simeq E$ for estimates, since at lower temperatures, where the doublet exists, the activation energy is probably higher (see the data of Ref. 8 for various temperatures). Nevertheless, the estimates which have been made clearly confirm the validity of the interpretation proposed here for the observed effect.

In summary, the disappearance of a doublet fine structure from the luminescence spectrum of a probe ion has been observed experimentally, with essentially no broadening of lines. This effect can be interpreted unambiguously as a manifestation of a dynamic averaging between two cation configurations which are realized as the result of rapid transitions of one of the ions in a classical two-well potential. It has thus become possible to show, for the first time, that the model of a two-level system can be applied to a superionic conductor.

We would like to take this opportunity to thank Yu. M. Gal'perin for a discussion of the results and B. P. Zakharchenya for interest in this study.

¹M. B. Salamon (editor), *Physics of Superionic Conductors*, Zinatne, Riga, 1982, p. 315.

²Mohua Mokur and Sujata Ghosh, *J. Phys. (Paris)* **59**, 431 (1989).

³M. E. Kompan and G. B. Venus, *Fiz. Tverd. Tela (Leningrad)* **32**, 11 (1990) [*Sov. Phys. Solid State* (to be published)].

⁴Yu. M. Gal'perin, V. L. Gurevich, and D. A. Parshin, *Zh. Eksp. Teor. Fiz.* **87**, 2178 (1984) [*Sov. Phys. JETP* **60**, 1259 (1984)].

⁵N. Gauthier and M. B. Walker, *Can. J. Phys.* **54**, 9 (1976).

⁶M. E. Kompan, G. B. Venus, and O. V. Dimitrova, *Fiz. Tverd. Tela (Leningrad)* **30**, 2454 (1988) [*Sov. Phys. Solid State* **30**, 1413 (1988)].

⁷M. E. Kompan, *Fiz. Tverd. Tela (Leningrad)* **31**, 79 (1989) [*Sov. Phys. Solid State* **31**, 1882 (1989)].

⁸V. I. Ponomarev, O. S. Filipenko, A. N. Chekhlov, and L. O. Atovmyan, *Khim. Fiz.* **21**, 1603 (1983).

Translated by D. Parsons