Photoluminescence of low-temperature phase of the superionic conductor $RbAg_4I_5$

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Results are presented of an experimental investigation of the superionic conductor $RbAg_4I_5$ by luminescence methods. The photoluminescence spectra of single-crystal and polycrystalline samples are obtained in the temperature range 10–300 K, the temperature dependence of the luminescence-line intensity is investigated, and the damping times are measured. The possible nature of the observed luminescence lines is discussed, as is the manifestation of the influence of the mobile-ion subsystem on the electron-hole subsystem.

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1. INTRODUCTION

Superionics, or solid electrolytes, are known as materials used as high-capacity solid-state current sources; a large number of unusual properties has made them recently the object of most active study. Typical examples of substances of this group are the complex salts MAg_4I_5 (where $M = K$, Rb, Sc, or NH_4), among which $RbAg_4I_5$, which has the maximum ionic conductivity at room temperature, is one of the most intensively investigated superionics.

At room temperature, $RbAg_4I_5$ belongs to the space group $P4_132(O^7)$ or $P4_332(O^6)$ (Ref. 1). The unit cell is a cube with edge 11.24 Å and contains four formula units of the salt. The regular crystals lattice consists in this case of rubidium and iodine ions, whereas 16 Ag^+ ions of the unit cell are almost completely disordered over the 56 possible positions. From among the four crystallography nonequivalent types of sites for the cations Ag^+ one must single out the sites at the centers of the tetrahedra made up of the iodine anions. In the α phase of $RbAg_4I_5$, such tetrahedra, which have common faces, form in the crystal a three-dimensional network. Since the energy barrier between two neighboring tetrahedral positions is relatively low, ~ 0.1 eV, the hopping of the Ag^+ ions over these positions takes place at room temperature with a frequency of the order of 10^{11}–10^{12} sec^{-1} (Ref. 2), and it is this which determines the high ionic electric conductivity of $RbAg_4I_5$.

When the temperature is lowered, at 209 K, a transition from the α to the β phase takes place in the crystal, and at 122 K there is a transition from the β to the γ phase, accompanied by a decrease of the conductivity by two orders of magnitude. It is important that in the β phase $RbAg_4I_5$ is macroscopically inhomogeneous, as noted already in Ref. 1. The lattice change accompanying the α–β transition is equivalent to its compression along a body diagonal of the cube, and in the phase transition there are produced in the crystal domains oriented along the four possible directions of the [111] axes of the crystal.

Although $RbAg_4I_5$ is not regarded as superionic in the low-temperature γ phase, the existing experimental data on the heat capacity and on the widths of the spectral lines,[3] and x-ray structure investigation data,[1] point unambiguously to the presence of disorder in the Ag^+ cations also at temperatures substantially lower than the phase-transition temperature 122 K.

The properties of the electron system of $RbAg_4I_5$ (as well, incidentally, of most superionic systems[4]) have been relatively little investigated. There are no reliable data on the electronic electric conductivity, no detailed investigations were made of the absorption edge, and investigations of the luminescence were barely initiated.[5] To our knowledge, only in Ref. 3 is the question of the singularities of the properties of the electron-hole subsystem in superionic crystals was formulated in explicit form, and the results of the experimental investigations of the exciton-reflection line widths were interpreted as observation of the influence of the disorder of the system of the Ag^+ cations on the properties of the excitations of the electron subsystem.

Obviously, the mutual influence of the electron subsystem and the subsystem of mobile ions does not reduce merely to a broadening of the lines of the electron-optical transitions. First of all, the superposition of the regular crystal structure of the I^- and Rb^+ ions on the disorder of the Ag^+ ions should lead to the appearance, in the forbidden band of the crystal, of tails of the density of states (this was pointed out to us by B. Z. Spivak), as is well known for amorphous solids and, to a lesser degree, for semiconducting solid solutions.[6] As a result of this one can expect a number of singularities in the properties of the electron subsystem. We note that, in contrast to the aforementioned bodies, in solid solutions the degree of disorder of the mobile sublattice of superionics depends on the temperature, making it possible to carry out investigations with continuous variation of the degree of ordering.

The anomalously high mobility of one of the species of crystal ions should lead to strong effects of the polaron type and, if the temperature is not too low, a new heretofore not considered mechanism of polaron screening may turn out to be significant. The number of possible positions of the Ag^+ cations in $RbAg_4I_5$ is much larger than the number of cations themselves, and the screening of a free electron or hole in the crystal can be due also to a change in the population of the cation positions near the carriers. This screening mecha-

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nism was not considered for solids, although it is a direct analog of Debye screening.

For the superionic conductor $RbAg_4I_5$ one might expect one other effect connected ith the partial redistribution, in the phase transitions, of the Ag^+ cations among positions with different symmetry. This should lead in principle to a redistribution of the intensities of the optical transitions connected with the given species of ions.

However, the characteristic time between hops of the Ag^+ cations is comparable with (and at room temperature much less than) the time of the allowed optical transitions. The experimental data[2] offer evidence that the time of "flight" over the intermediate positions is of the same order as the lifetime in a definite position. Therefore, even if account is taken of only the most probable hopping between equivalent (tetrahedral) positions, the optical-transition lines should be substantially broadened by the frequent change of symmetry of the surrounding of the Ag^+ cations. Thus, it is precisely the high mobility of the Ag^+ cations which make observation of similar effects unlikely.

EXPERIMENT

1. We have investigated the photoluminescence of purposefully undoped samples of $RbAg_4I_5$. In most experiments the luminescence was excited by short (10 nsec) pulses from a nitrogen laser. The photon energy of the exciting light was 3.68 eV, which exceeds by 0.5 eV the width of the forbidden band in the investigated substance. The power density of the exciting light in the pulse varied in a wide range from several watts to dozens of kilowatts per mm^2. In some experiments, luminescence was excited by light from individual spectral lines of a mercury lamp or an incandescent lamp and the necessary spectral regions were separated with a monochromator. The spectra obtained in these experiments had a lower signal/noise ratio and were not substantially different from the data given in the article and obtained with laser excitation. The spectra were recorded in the range 3.33–1.5 eV. The experimental technique was described in greater detail in Ref. 5.

The luminescence was observed by us for different types of samples. We had at our disposal single crystals grown by the isothermal method from a solution of AgI and RbI in acetone.[13] The single crystals were optically transparent, practically colorless, with good natural faceting. Special methods of purification and optimal conditions of crystallization made it possible to lower the content of Mn, Mg, Pb, Fe, and Ni in the single crystals to 10^{-4} wt.%. The ionic conductivity measured in the alternating current was 0.3 $\Omega^{-1}\cdot cm^{-1}$, thus attesting to a high quality of the investigated single crystals. In addition, the investigations were performed on polycrystalline samples obtained by the Czochralski method from the melt, on chemically synthesized powders, and on pellets pressed from them. The surface of the crystalline samples was ground directly prior to the experiment and the next polished with diamond paste, and the surfaces of the pellet samples were cleaned with dry abrasive.

2. Samples of undoped $RbAg_4I_5$ were luminescent in the wavelength region from 375 to 500 nm. A typical spectrum is shown in Fig. 1. At high temperatures (in the α and β phases) the luminescence spectra of all the investigated samples consisted of a single line with a maximum near 428 nm and with a half-width of the order of 6 nm (lower curve of Fig. 1). At low temperatures, the observed spectra consisted of broad bands and relatively narrow lines, while the spectra of the powders and of the crystalline samples differed noticeably. In Fig. 1 the luminescence spectrum of the crystal is represented by the upper solid curve, and the luminescence of the powdered sample by the dashes line. At temperatures below 40 K one observes on the short-wave edge of the spectra a line with a maximum at 377 nm. This line is narrower and more intense in luminescence spectra of the less perfect samples—powders, pellets, crystals that have become turbid as a result of prolonged storage in air. In the spectra of high-grade single crystals, at low excitation intensity, the 377 nm line was practically unobservable. The broad band with maximum near 390 nm is present in the spectra of all the samples and is practically the only one at low excitation intensity in the luminescence of high-grade crystals. The maximum intensity of this band is shifted towards 400 nm when the temperature is raised from 8 to 70 K. It should be noted that upon repeated cooling of the samples to liquid-helium temperature the shape of the 390-nm band was not always strictly reproducible, apparently because of the presence of inhomogeneous strains in the samples after the phase transition.

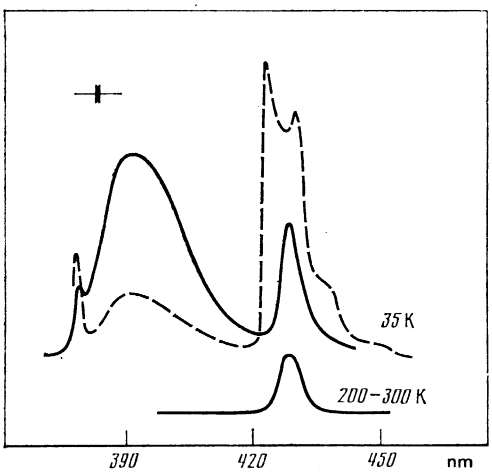

FIG. 1. Luminescence spectra of the ionic conductor $RbAg_4I_5$. Upper solid line—crystal, dashed—luminescence of powder.

In the 420–500 nm region, the luminescence spectra of single crystals have only one line at 428 nm. For less perfect samples it is possible to separate narrow maxima at 424 and 430 nm and two relatively braod bands with centers at 437–440 and near 450 nm. The intensity ratio in this spectral region varied from sample to sample. On the right side of Fig. 2 is shown the evolution, with temperature, of a section of the spectrum near the 424–430 nm doublet. In the left part of the figure is shown the dependence of the positions of the lines on the temperature. It can be seen that there is a certain correlation between the positions of the lines 424 nm and 430 nm on the one hand, and the phase transitions in the $RbAg_4I_5$ investigated by us on the other. For the single–

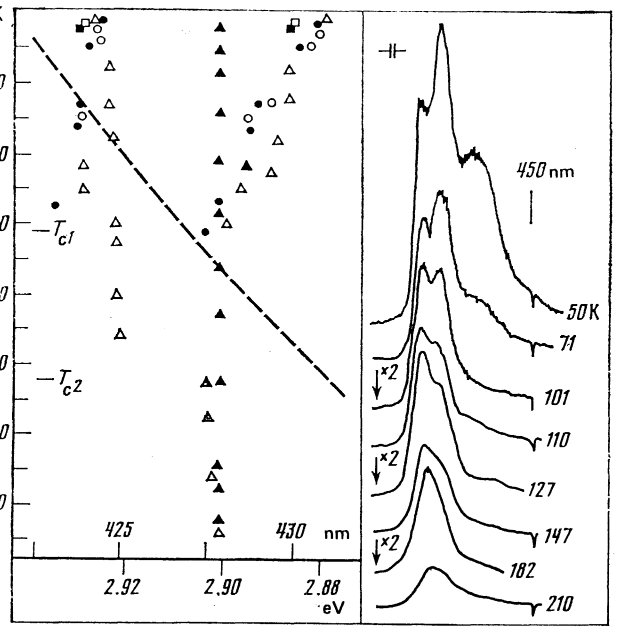

FIG. 2. Right—evolution with temperature of a section of the luminescence spectrum of a pellet in the 420–450 nm region. In the places marked by arrows, the scale of the curves in the vertical direction is doubled to compensate for the decrease of the intensity of the lines with temperature. Left—dependence of the line positions on the temperature. Dashed line—dependence of the width of the forbidden band of silver iodide on the temperature[3]; ▲—position of the luminescence band in single crystals. The remaining symbols mark different pellet samples.

crystal samples, the luminescence line 428 nm does not change its position in the entire temperature range from room temperature to that of liquid helium.

The intensities of all the luminescence bands decreased with increasing temperature. As can be seen from Fig. 3, in the region from helium temperatures to 70 K, the decrease of the intensity was close to linear.

We have also measured the damping times for different luminescence lines. For all the lines we observed times of the order of 10^{-8} sec, which corresponds to allowed optical transitions. The maximum emission time, 50 nsec, was recorded for the 450 nm band, and the minimum, approximately 12 nsec, for the 377 nm line, the latter being mainly determined by the time or decay of the excitation pulse. For the 390-nm band, the decay time was different for the shortwave edge, for the center, and for the long-wave edge, and amounted to 16, 20, and 28 nsec, respectively.

DISCUSSION OF RESULTS

1. We consider first the possible nature of the broad luminescence bands. The band with the maximum near 390 nm predominates in the spectra of single crystals. Its position is close to the known position of the absorption edge in films of the investigated substance,[8] and the temperature shift corresponds to a decrease of the width of the forbidden band of the crystal when heated.[3] These facts enable us to connect the 390 nm bands with the edge radiation of the crystal, although the available data are undoubtedly sufficient to be able to propose some concrete schemes of recombination via bound excitons or via shallow impurities near the band edge.

Some of the luminescence bands in the 420–500 nm region are connected with defects in the investigated samples. For the hexagonal modification of silver iodide, traces of which can always be assumed to be present in the investigated substance, two bands are distinguished: edge luminescence with a maximum near 425 nm (we shall not consider the detailed structure of this band) and radiative recombination via an acceptor—cation vacancy with maximum near 450 nm (Ref. 9). Such bands were observed by us in the least perfect samples. A band with a maximum at 440 nm is observed in the spectra of $RbAg_4I_5$ powders and in the pellets pressed from them. The luminescence spectra of single crystals, the appearance of a similar band could be attained after prolonged preliminary illumination of the sample with intense white light. This makes it possible to connect the given band with radiative recombination via the photodegradiation centers of the material, and most probably via donors—anion vacancies.

The positions of the narrow lines 377, 424, and 430 nm in the luminescence spectra of $RbAg_4I_5$ coincide with the positions of the known exciton transitions. The 377-nm line coincides with the maximum on the fundamental absorption edge of thin films[8] and with the exciton reflection line[3] in $RbAg_4I_5$ at low temperatures. The maxima 424 and 430 nm coincide with the positions of the exciton-luminescence lines in 2H- and 4H-polytypes of β-AgI (Ref. 7). In our case, however, all these lines are observed in spectra of samples that are known to have defects, and do not occur in single crystals. The temperature dependence of the positions of the narrow lines does not correspond to the available published data on temperature dependence of the widths of the forbidden bands in $RbAg_4I_5$ and β-AgI (Ref. 3). These additional facts, in our opinion, do not allow us to interpret, on the basis of only the equality of the energies, the observed narrow lines as corresponding exciton transitions.

There exists a possibility of explaining the behavior of the narrow lines in the luminescence spectra of the low-temperature modification of the superionic $RbAg_4I_5$ on the basis

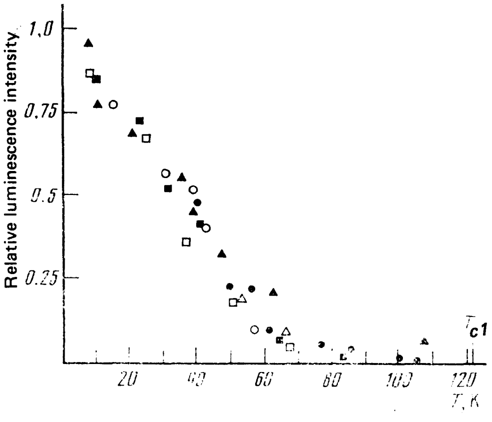

FIG. 3. Dependence of the intensities of different luminescence lines of $RbAg_4I_5$ on the temperature: □, ■—440 nm band, ○,●—390 nm, △—437 nm, ▲—428 nm line.

of a single model. This model is based on a hypothesis advanced long ago by Seitz,[10] that the band observed in the vicinity of 425 nm at the edge of the fundamental absorption of AgI is connected with the transitions $4d^9 5s^{-1} - 4d^{10}$, which are forbidden in the free ion and which can be allowed for an ion in a tetrahedral coordination. This viewpoint is accepted in modern papers, e.g., in Ref. 8, whose authors interpret the 425-nm band in the absorption spectra of $RbAg_4I_5$ in similar fashion. Within the framework of this approach, all three narrow lines observed by us in the luminescence spectra constitute transitions of the Ag^+ ions from sublevels of the excited state $4d^9 5s^1$ to the ground level $4d^{10}$ (the level scheme for the Ag^+ ion is given in Ref. 10). This approach explains in natural fashion the absence of temperature shifts in the positions of the luminescence lines, since an excitation localized on the ion (i.e., a small-radius exciton) hardly feels the change of the crystal lattice with changing temperature. On the basis of this model it is possible to explain qualitatively also the difference between the luminescence spectra of perfect and imperfect samples. In perfect samples, the silver ions are more mobile (we recall that it is precisely the jumps of the silver ions between the tetrahedral positions which determine the high ionic electric conductivity of superionics). The symmetry of the surrounding of the Ag^+ ion changes quite frequently, and the transition lines should be broadened. It can also be assumed that the probability of localization of the excitation on an individual ion is less for ions with high mobility. In less perfect samples near the disturbances of the normal structure of the crystal, the Ag^+ cations are localized and the transitions discussed should produce sharp and more intense lines in full accordance with what is observed in experiment. In order for such transitions to become observable, the Ag^+ ions in the excited state $4d^9 5s^1$ (with electron-hole on the d levels) should be produced as a result of the action of the exciting light. For example, (see Fig. 4), the p–d transition of the electron from the d-shells of silver to a previously produced (by another photon) electron hole at the top of the valence band. The presence of such a two-step ionization mechanism should manifest itself in the dependence of the luminescence intensity on the excitation intensity. The exponent in this dependence should be higher for bands due to two-step excitation, although its concrete value can depend on the details of the recombination process. Growth of the intensity of narrow luminescence bands in advance of the broad ones was indeed observed by us earlier,[5] but without a suitable interpretation.

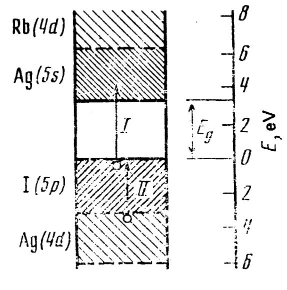

FIG. 4. Suggested band scheme of $RbAg_4I_5$ at room temperature.[3] I—excitation of electron at fundamental absorption, II—excitation of electron from d-shells of silver ion into an occupied state in the top of the valence band.

An additional confirmation of the intra-ion character of the observed transitions is the presence of a similar doublet near 425 nm in the luminescence of the silver-containing crystal K_2AgI_3 (Ref. 11). We have observed at room temperature a 428 nm line in the luminescence spectrum of single-crystal RbI: 0.5 mol.% AgI; this line coincides with the corresponding line of $RbAg_4I_5$.

2. The decrease of the luminescence intensity with temperature is a rather common phenomenon. In silver halides, an exponential extinction law was observed, due to the activating character of the nonradiative transitions.[9] In our case, in the temperature region from liquid helium to 70 K, the intensity decreases monotonically in nearly linear fashion. Attention is called to the agreement between the dependences for the different lines—for the 428 nm line, which is most readily in the observed spectra a superposition of several lines, for the 390 nm band which is due to edge emission, and for the 440 nm band, which is due to recombination via photodegradation center. It is reasonable to assume that the cause of such a behavior is the action of a certain common nonradiative-recombination mechanism on the free electrons or holes. Such a mechansim in substances with high ion mobility can be the screening of the electrons or holes by the mobile ions. Screening weakens the Coulomb interaction between the electrons and holes, and this should lead to a decrease in the radiative-recombination probability.

Two other experimental facts find a natual explanation within the framework of the advanced hypothesis concerning the possible mechanism of nonradiative recombination.

The 390 nm luminescence band shifts towards 400 nm when the temperature is rasied to 70 K, i.e., by 75 meV, whereas according to the data of Ref. 3 the decrease of E_g in this temperature interval, determined by measuring the reflection spectra, amounted to 25–30 meV. This corresponds to an increase, with rising temperature, of the energy gap between the bottom of the conduction band and the level from which the electron recombines.[1)]

Let the difference $\Delta E \approx 50$ meV in the displacements be the depth of the polaron well produced by the ion screening. We can estimate the radius of the localized state of the electron in such a well: $r \approx e^2/2\varepsilon\Delta E$, which amounts to 50 Å at $\varepsilon \sim 5$. At an average distance 5 Å between the possible locations of the silver, such a region contains 10^3 positions of Ag^+ cations. This estimate shows that the region of localization contains a large number of possible positions of mobile ions and the screening can be due to a change in the population of these locations.

It is important that the process of screening electrons by hopping ions is a rather slow process at least at low temperatures, when the time between the hops can be longer than the time of luminescence emission. The most interesting is the temperature region in which the luminescence emission time is of the order of the time between the ion hops. In this case the longer the lifetime of the electron and of the hole from creation to recombination, the smaller the energy of the recombination-radiation photon. Under pulsed excitation it is possible in principle to expect a time shift of the luminescence line, after excitation, in the red direction. When measuring the fluorescence damping times, the corresponding times should be shorter for the shorter-wave edge of such a line and longer for the long-wave edge. This was indeed observed by us for the 390 nm band. Such an observation is evidence in favor of the hopping mechanism of screening, inasmuch as screening by ions that move in the lattice should take place over times of the order of the period of the optical lattice vibrations.

It is possible to interpret the three basic experimental facts discussed in the present section (the common temperature dependence of the intensity of the luminescence lines, the anomalously large temperature shift of the 390-nm line, the different damping times along its contour) also on the basis of the model of the tails of the density of states. The density of state in the forbidden band should increase with increasing temperature, owing to the growth of the disorder of one of the ionic sublattices. The presence of a background of the density of states in the forbidden band should facilitate the nonradiative recombination, in qualitative agreement with experiment. At first glance the observed shift of the 390-nm band is more readily evidence against the "tail" model, inasmuch as the population of the states with high energy increases with increasing temperature, and the observed shift should be "blue." Such an effect was recently observed in solid solutions of semiconductors.[12] In our case, the band shifts in the opposite direction, but this can be due to the fact that the shape of the tails of the density of states also changes with temperature. This assumption is natural for superionics, since the degree of disorder in them depends essentially on the temperature. The difference between the luminescence emission times along the band contour is not a direct consequence of the discussed model, and to explain this fact it is necessary to introduce additional assumptions. The present paper reports the first investigation of the superionic conductor $RbAg_4I_5$ by luminescence methods. The spectra obtained for samples prepared in different ways agree well with one another and with those observed in our first study.[5] The interpretation of the luminescence spectra corresponds to the published data on absorption[8] and reflection,[3] and takes into account the singularities of spectra of different samples. The proposed variant of the interpretation seems to us more probable but one cannot exclude the possibility that the observed anomalies of the behavior of the luminescence lines are due to action of inhomogeneous stresses in the sample. To choose the final variant of the interpretation it is necessary to investigate the optical properties under pressure. We have also attempted to take into account the influence of the mobile ion subsystem on the electron-hole subsystem. Two basic mechanisms of such an influence, discussed in the present article, namely, screening by mobile ions and tails of the densities of states in the forbidden band, are not mutually exclusive. In our opinion, the aggregate of the experimental facts can be explained more consistently on the basis of the screening model.

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[1)] Data that might enable us to speak in the present case concretely of an electron or hole polaron are absent. We left out the analogous reasoning for holes, to avoid repetition.

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