Ion screening and radiative recombination of localized carriers in the low-temperature phase of the ionic conductor RbCu$_4$Cl$_3$I$_2$

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Sharp changes in the characteristics of the luminescence band with a photon energy of 2 eV have been observed in the γ phase of the superionic conductor RbCu$_4$Cl$_3$I$_2$ at 60 K. It is suggested that the observed anomaly results from a change in the structure of the ion subsystem near the charged center which is responsible for the radiative recombination.

The high ionic electrical conductivity of superionic conductors should result in many optical effects by virtue of the Coulomb interaction between the ion and electron current carriers. The electrons and holes produced during interband absorption of light are not equilibrium carriers, and their appearance should cause a redistribution of the equilibrium carriers: mobile ions. The simplest situation should arise during the localization of photoexcited charges; in this case the ions should screen the immobile charged centers that form. The changes in the surroundings of the center and in its effective charge which result from the screening should be manifested as changes in the spectral and kinetic characteristics of the luminescence bands associated with recombination at this center.

It should be noted, however, that the high-temperature phases of ionic conductors, which are superionic conductors in the strict sense of the term, are inconvenient for the observation of effects of this sort. The ionic conductivity in this case is too high, and the screening of the center occurs too rapidly. As an estimate of the scale time of the screening we can use the Maxwellian time $\tau_M = \epsilon\epsilon_0/\sigma$, which is a measure of the rate of dissipation of nonequilibrium charge (σ is the conductivity, and $\epsilon\epsilon_0$ is the absolute dielectric constant), or we could use the average time for the hop of a mobile ion between allowed positions. For α-RbAg$_4$I$_5$ or α-RbCu$_4$Cl$_3$I$_2$, for example, we find estimates on the order of 10^{-11}–10^{-12} s by either approach; these times are many orders of magnitude shorter than the typical microsecond-range times for radiative recombination involving a center. In this case the center is always manifested as a "screened" center in the luminescence.

The low-temperature phases of superionic conductors, which have a high resistivity and thus are not regarded as superionic conductors, nevertheless have a low activation energy for ionic conductivity (0.31 eV for γ-RbCu$_4$Cl$_3$I$_2$; Ref. 1) and a high carrier density, on the order of 10^{22} cm^{-3}. For this particular combination of parameters, an ionic mobility and an ionic screening are still possible, but these processes are considerably slower. Depending on the temperature, the centers of a certain type may be

o – RbCu$_4$Cl$_3$I$_2$:S
+ – RbCu$_4$Cl$_3$I$_2$:Cu

Wavelength, nm

625

600

575

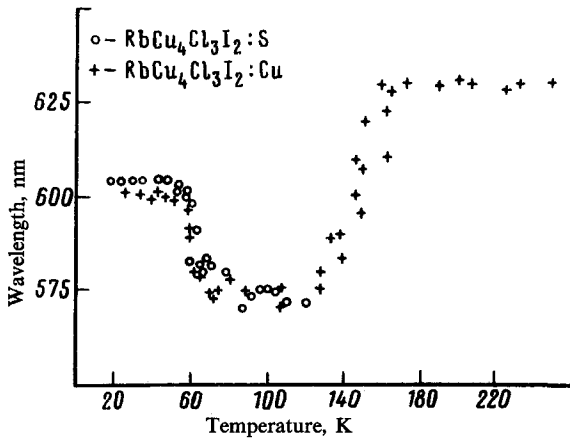20   60   100   140   180   220

Temperature, K

FIG. 1. Spectral position of the luminescence band versus the temperature in time-integrated measurements.

predominantly screened or unscreened at the time of recombination. It thus becomes possible to observe effects that result from an ion screening of the centers, by detecting the temperature dependence of the characteristics of the recombination radiation.

We have previously[2] observed a luminescence in the red region in a study of the luminescence of the solid electrolyte RbCu$_4$Cl$_3$I$_2$, whose conductivity stems from the copper ions. In the present letter we report a study of this red luminescence at temperatures, below 170 K, i.e., in the low-temperature γ phase. We have discovered a sharp change in the spectral position of the band at about 60 K. Figure 1 shows the temperature dependence of the position of the band peak. We interpret the change in the position of the peak over the temperature interval 110–170 K as the quenching of one of two components of a composite luminescence band as a phase-transition temperature is approached.[2] We see that the change near 60 K is substantially sharper than that near the known phase transition at 170 K. The spectral behavior of the band at 60 K is the same for the two types of samples in these experiments: samples doped with sulfur, with a concentration on the order of 1%, and samples containing an excess of metallic copper. We observed no sharp changes in the characteristics of other bands in this temperature range.

To determine the nature of this phenomenon, we carried out time-resolved measurements of the luminescence spectra in the pertinent region. For this purpose the luminescence was measured over a short time interval (4 ns) at an adjustable delay with respect to the excitation pulse. We found that in this case we do not see a single temperature for the anomaly (Fig. 2): At a short delay of the measurement interval with respect to the excitation pulse, the observed change in the position of the band occurs at a relatively high temperature, ~100 K, while in the case of a long delay the change occurs at temperatures substantially lower, ~60–70 K. The observation of a shift in the temperature at which the anomaly is observed during time-resolved measurements of the luminescence gives us important information for interpreting this phenomenon.

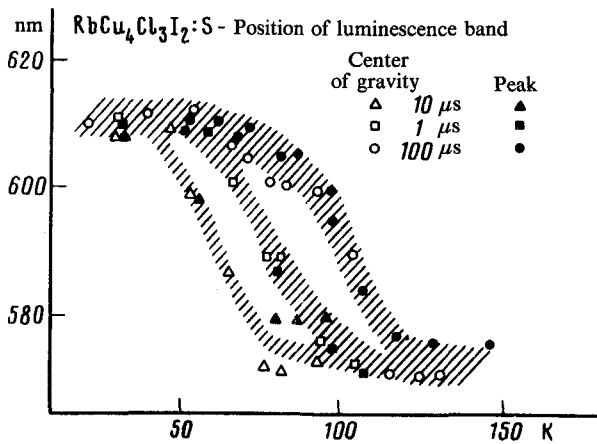We first note that no data have been published on the conductivity or structure of

nm | $RbCu_4Cl_3I_2:S$ - Position of luminescence band

FIG. 2. Positions of the luminescence band in the temperature range 20–150 K according to time-resolved measurements.

$RbCu_4Cl_3I_2$ for temperature $T < 120$ K, so that this anomaly may be a manifestation of an unknown phase transition. The absence of sharp changes in the parameters of the other luminescence bands, however, does not support this interpretation. A more likely explanation is that we are observing local changes near emission centers. The data from the time-resolved spectroscopy—the dependence on the delay time—clearly show that we are observing not a change in the properties of the material at some temperatures but a faster or slower response to the excitation pulse, depending on the temperature.

Some rough calculations demonstrate the plausibility of this interpretation—a change in the ion surroundings of a center. We first note that at the carrier densities on the order of 10^{22} cm^{-3} in superionic conductors and at temperatures ~ 100 K the Debye formula yields a screening radius on the order of 1 Å. This result shows that the individual centers must be screened by ions if the lifetime is substantial. The temperature range in which the screening should be manifested most obviously in the luminescence can be determined by equating the lifetime of an electron with respect to recombination at a center to the response time of the subsystem of mobile ions. It must be taken into account, however, that near a charged center the Coulomb field is superimposed on the potential relief of the ion diffusion paths, so that the activation energy for the hops of ions along certain directions, not too far from the center, may be very different from that expected from data on the conductivity. It is simple to show that for γ-$RbCu_4Cl_3I_2$ at a distance of 50 Å from a center with a charge e, for example, the activation energy is reduced by a factor of about two. In the estimate of the Maxwellian time, we use data on the conductivity which presuppose an undistorted activation energy. For this reason, the temperature estimated by equating the lifetime to the Maxwellian time, $\tau_l = \tau_M(T)$, is an upper estimate of the temperature at which the center is screened. Assuming $\epsilon \sim 10$ and using conductivity data from Ref. 2, we find an upper estimate of the temperature at which the screening of a center will be manifested for a lifetime $\tau_l = 1$ μs: $T_{scr} < 120$ K. The results of this estimate agree well with the data in Fig. 2. The lower temperature of the anomaly for the time-integrated

spectra is attributed to the substantial emission due to the slowest components of the composite band.

At this point, we can offer only some general suggestions regarding the mechanism for the effect of a change in the structure of the mobile ion subsystem on recombination processes. In particular, on the basis of the data presently available we cannot say whether the centers that luminesce at temperatures above the anomaly are "screened analogs" of centers that luminesce at a low temperature, or whether the emission in different temperature regions is by centers of different types. However, the mechanism of screening by mobile ions proposed by us here to explain the experimental data should be general in nature and should be manifested in a variety of optical and photoelectric experiments.

[1]S. Geller, J. R. Akridge, and S. A. Wilber, Phys. Rev. B **19**, 5396 (1979).
[2]M. M. Afanas'ev, G. B. Venus, O. G. Gromov, M. E. Kompan, and A. P. Kuz'min, Fiz. Tverd. Tela (Leningrad) **26**, 2956 (1984) [Sov. Phys. Solid State **26**, 1785 (1974)].