

## Raman effect in additively colored superionic $\text{RbAg}_4\text{I}_5$ single crystals

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The method of Raman scattering is used to show that chemical injection of holes into the volume of superionic  $\text{RbAg}_4\text{I}_5$  leads to the synthesis of iodine molecules  $\text{I}_2$  from the intrinsic iodine anions of the crystal lattice.

The compound rubidium-silver penta-iodide ( $\text{RbAg}_4\text{I}_5$ ) is the best-known and one of the principal compounds used in the technology of superionic materials. Goffman *et al.*<sup>1</sup> discovered that this material becomes additively colored in iodine vapor. Using radioactive isotopes, they also showed in the same study that the high rate of penetration of color into the sample is not related to the diffusion of elemental iodine into the body of the sample, since the diffusion coefficient is too low ( $\leq 10^{-2} \text{ cm}^2 \cdot \text{sec}^{-1}$  at  $140^\circ\text{C}$ ). The following model of the additive coloring process was proposed: Some of the cations of the "moving"  $\text{Ag}^+$  sublattice diffuse to the surface and bond chemically to free iodine to form nonsuperionic silver iodide on the surface. Electrical neutrality is ensured by diffusion of electron holes from the surface into the volume of the crystal. Essentially, surface treatment with iodine vapor results

in injection of electron holes into the volume. By analogy with alkali halide crystals, it was assumed that hole can be localized on a cation vacancy to form  $V_c^+$  centers.

The model was partially confirmed by luminescence experiments: It was shown that additive coloring results in the formation of an easily removable layer of silver iodide, mainly of the  $\beta$  modification.<sup>2</sup> In addition, a study<sup>3</sup> against the background of the intrinsic absorption edge, it was possible to distinguish a band formed during coloring in the 3.2 to 2.4-eV range, but specific data that would help to determine the nature of the color centers were not obtained.

We postulated that in superionic conductors the anionic sublattice of iodine ions, which is considered rigid, should have some mobility. This may lead to localization of a pair of electron holes  $h^+$  on a pair of  $I^-$  anions that have come close together. Formation of such a center could be detected from the presence of the corresponding molecular vibrations, for example, in Raman spectra. An indirect confirmation of the

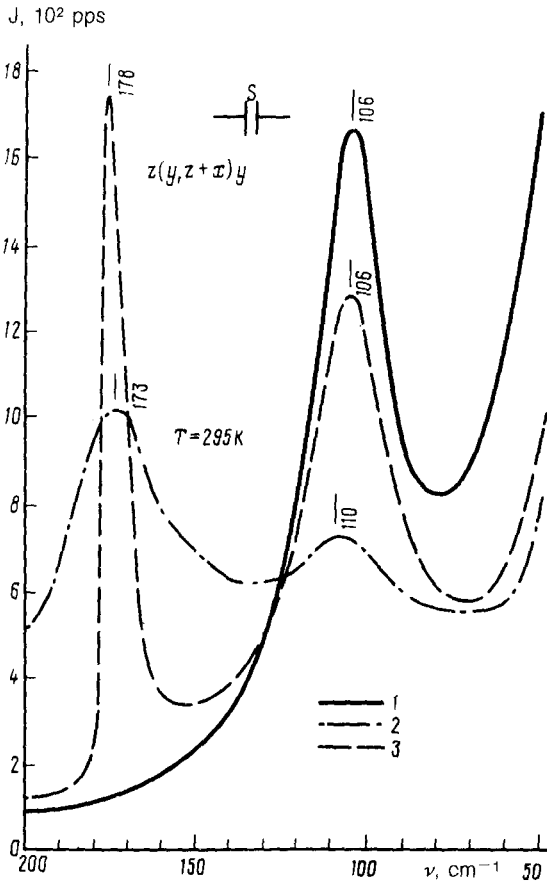


FIG. 1. Raman spectra in  $Z(Y, Z + X)Y$  geometry at room temperature. 1—Spectrum of initial  $RbAg_4I_5$  crystal (amplitude reduced fivefold); 2—spectrum of crystalline iodine; 3—spectrum of additively colored crystal.

validity of this hypothesis was the coincidence of the spectral ranges of optical absorption in the additively colored material and molecular iodine.

We used  $\text{RbAg}_4\text{I}_5$  single crystals grown isothermally from acetone solution. The single crystals to be used in the experiments were polished parallel to the  $\langle 110 \rangle$  natural faces.

The Raman spectra were excited with an LG-38 He-Ne laser ( $\lambda = 6328 \text{ \AA}$ ;  $W = 30 \text{ mW}$ ) and analyzed with SPEX-RAMALOG 5 spectrometer in  $90^\circ$  scattering geometry. The experiments were conducted at room temperature.

The results of the experiments are shown in the figures. Curve 1 of Fig. 1, which corresponds to the spectrum of the initial sample, is analogous to the known Raman

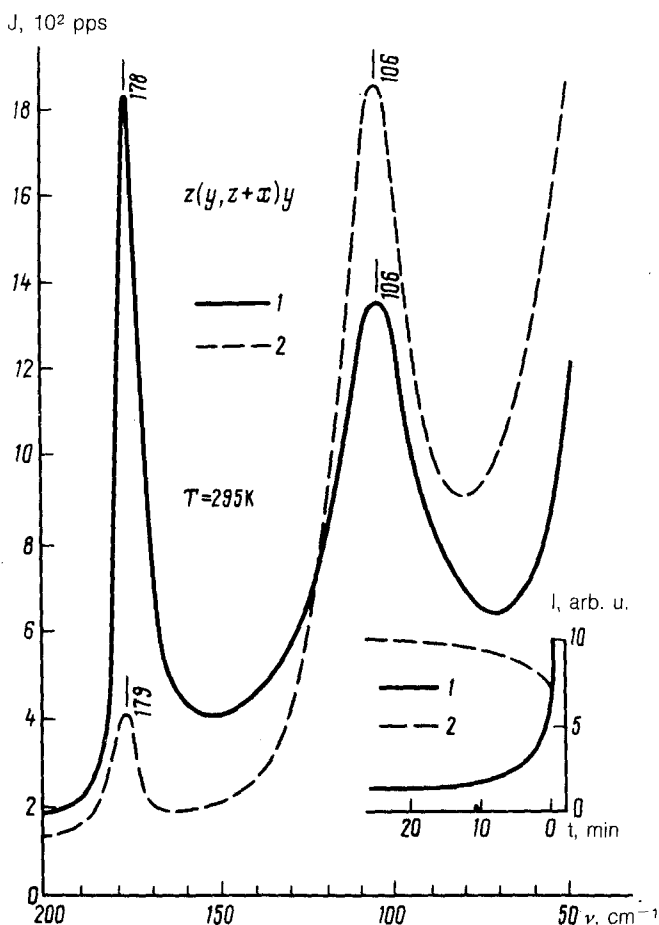


FIG. 2. Time evolution of the Raman spectrum of additively colored  $\text{RbAg}_4\text{I}_5$  crystal. 1—Spectrum in the first recording; 2—recording after 30 min of exposure of the crystal to a laser beam. Inset: change of scattering intensity with time: 1—at a frequency of  $178 \text{ cm}^{-1}$ ; 2—at a frequency of  $106 \text{ cm}^{-1}$ .

spectra for the superionic phase of  $\text{RbAg}_4\text{I}_5$ . As we know, the line ( $106\text{ cm}^{-1}$ ) observed at these temperatures corresponds to the totally symmetric breathing vibrations of iodine tetrahedra.<sup>4</sup> Curve 2 represents the Raman spectrum of crystalline iodine, which we obtained for comparison.

The appearance of the spectrum for adequately colored crystals depends on the color intensity. For slightly colored crystals, no appreciable differences from the spectra of the initial crystals were observed. For crystals with an intense (light-brown) color, a new line near  $178\text{ cm}^{-1}$  was clearly observed in the Raman spectra (curve 3 in Fig. 1). We note the appreciable intensity of this line and its small width in comparison to the lines corresponding to the crystal lattice vibrations. Moreover, the spectrum similar to curve 3 in Fig. 2 was essentially unstable in time: Under the conditions of the experiment, the signal in the  $178\text{ cm}^{-1}$  line decreased by approximately an order of magnitude after the first ten seconds of exposure. We also observed a certain increase of intensity in the  $106\text{-cm}^{-1}$  line, apparently because of an increase in the transparency of the sample as a whole. The time evolution of the spectra is shown in Fig. 2. As the intensity of the  $178\text{-cm}^{-1}$  line decreased, its slight shift ( $1\text{--}2\text{ cm}^{-1}$ ) into the high-frequency region was observed.

It is evident from Fig. 1 that the new line formed in the spectrum falls in the range of vibration frequencies characteristic of the crystalline form of molecular iodine. The corresponding spectral band for iodine which we analyzed was assigned to the intramolecular vibrations of the  $\text{I}_2$  dumbbell in the ground state, with allowance for the influence of the crystalline environment.<sup>5</sup> Thus, if the case of random coincidence is disregarded, it is necessary to acknowledge the formation of  $\text{I}_2$  molecules in  $\text{RbAg}_4\text{I}_5$  crystals at sufficient color intensity.

It may be assumed that the cause of the observed effect is trivial: Scattering could be observed on molecular iodine adsorbed on the surface or diffused into the crystal. To eliminate the first cause, we ground down the colored crystals before the experiment to a depth of  $\sim 0.5\text{ mm}$ . The signal was recorded in  $90^\circ$  geometry, with the beam passing at a depth of  $\sim 1\text{ mm}$  from the crystal surface. In addition, we were completely unable to detect the  $178\text{-cm}^{-1}$  line on the unpolished surface of the crystal which was treated with iodine vapor. The second cause could not have led to the observed effect either: The experiments were carried out on single crystals of the same runs for which the absence of diffusion into the volume was demonstrated by the radio-isotope method<sup>1</sup>; our samples were not cooled, which precluded the possibility of cracking during the phase transition  $\alpha \rightleftharpoons \beta$ , with subsequent penetration of iodine through the microcracks.

Thus, the most probable cause of the observation of the  $178\text{-cm}^{-1}$  line in the spectrum of additively colored single crystals is the synthesis of  $\text{I}_2^0$  molecular centers from the intrinsic anions of the lattice.

The proposed interpretation is in good agreement with the observed characteristics of the new line. The high intensity, despite the supposedly small number of centers,<sup>3</sup> may be caused by the resonance conditions of scattering; its relatively small width is naturally attributed to the local character of the corresponding vibrations. Some questions, such as how the Raman spectra depend on the concentration of the

centers and the nature of the photodegradation, have not been answered in this work and require further studies.

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<sup>1</sup> V. G. Goffman *et al.*, *Elektrokhimiya* **15**, 1252 (1979).

<sup>2</sup> M. M. Afanas'ev *et al.*, *Fiz. Tverd. Tela* **29**, 940 (1987) [*Sov. Phys. Solid State* **29**, 539 (1987)].

<sup>3</sup> V. N. Andreev and V. G. Goffman, *Fiz. Tverd. Tela* **25**, 3480 (1983) [*Sov. Phys. Solid State* **25**, 2004 (1983)].

<sup>4</sup> D. A. Gallagher and M. V. Klein, *Phys. Rev. B* **19**, 4282 (1979).

<sup>5</sup> J. R. Magña and J. J. Lanin, *Phys. Rev. B* **37**, 2475 (1988).

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