Excitons in a crystal with a superionic transition

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Indirect excitons are observed for the first time in the γ and β phases of the $RbAg_4I_5$ crystal. Estimates are given for the energies of formation of direct and indirect excitons in the γ phase. A study is made of the behavior of the excitons at the transition of the crystal to a disordered state.

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The classical superionic conductor $RbAg_4I_5$ exists in three modifications.[1] The transition to the superionic state, accompanied by an abrupt change in conductivity, occurs at 121.8 K. This transition is associated with a partial disordering of the crystal (a first-order transition of the order–disorder type). At 209 K there is a second-order[1)] phase transition $\beta \rightarrow \alpha$, which is accompanied by a relatively small change in conductivity and a complete disordering of the silver sublattice.

The low temperature of the superionic transition in $RbAg_4I_5$ makes this crystal a convenient object of study for investigating the effect of disordering on the excitonic states. In this study we have investigated the exciton spectra of $RbAg_4I_5$ in single crystals, which we grew from specially purified AgI and RbI in solution with HI by the method of Ref. 3, and also in polycrystalline films 0.5–2 μm thick. The excitonic transmission and reflection spectra were studied under steady-state and modulated conditions over the temperature range 4–295 K. The wavelength was modulated by the vibration of a flat quartz plate placed in front of the exit slit of a DMR-4 monochromator. The temperature-stabilizing system was capable of holding the temperature constant to within ± 0.5 K in the phase-transition region. The luminescence of the crystals was excited by a nitrogen laser with $\lambda_{exc} = 337$ nm.

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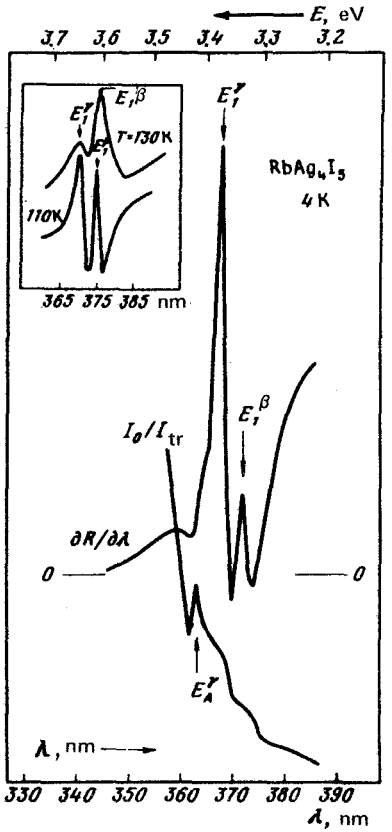

FIG. 1. The reflection spectrum in modulated incident light for a polycrystalline film of $RbAg_4I_5$ at various temperatures and the transmission spectrum at 4 K, in arbitrary units.

In the transmission spectrum of the films at 4.2 K (Fig. 1) one clearly sees two jogs of the sort which are characteristic of indirect excitonic transitions. The features in the transmission spectrum correspond to abrupt changes in the reflection spectrum for the modulated case. We attribute the clearest feature in the modulational reflection spectrum at $E_1^{\gamma} = 3.372$ eV and the corresponding jog in the transmission spectrum to an indirect transition to the excitonic ground state with the excitation of an optical phonon in the γ phase of $RbAg_4I_5$. In several of the films we were able to observe a splitting of the main peak of the modulational reflection spectrum.

If it is assumed that the exciton interacts with a 107-cm^{-1} phonon,[4] then the energy of formation of an indirect exciton in the γ phase is $E_{exc}^{\gamma} = 3.359$ eV at 4.2 K and $E_{exc}^{\gamma} = 3.346$ eV at 77 K.

In the region of high absorption, an asymmetrical line is observed in the transmission spectrum with a maximum absorption at $E_A^{\gamma} = 3.417$ eV, which we attribute to direct excitonic transitions in the γ phase.

In the single crystals we obtained the values $E_1^{\gamma} = 3.340$ eV and $E_{exc}^{\gamma} = 3.327$ eV, i.e., the spectrum in the films is shifted to shorter wavelengths by 0.032 eV.

The longest-wavelength jog and the corresponding feature in the modulational reflection spectrum, at $E_1^{\beta} = 3.329$ eV in Fig. 1, occupies a different spectral position in different films, over the range 3.329–3.344 eV. The intensity of this structure also varies from sample to sample, being largest in films that have been subjected to special quenching and annealing. We believe that this jog is due to indirect excitonic transitions in the high-temperature β phase,[2)] which can be present in small number in a "frozen-in" state in the low-temperature γ phase.[5] Lendign support to this point of view are the growth in the intensity of the E_1^{β} peak with increasing temperature (Fig. 1) and the different temperature shifts of the peaks $E_1^{\gamma}(1.7\times10^{-4}$ eV/deg) and $E_1^{\beta}(4.0\times10^{-4}$ eV/deg).

Similar features in the modulational reflection spectrum of $RbAg_4I_5$ were observed by Bauer and Huberman.[6] However, those authors did not study the transmission spectra and attributed all of the structure they had observed to direct excitonic transitions in γ $RbAg_4I_5$.

The half-widths of the peaks E_1^{γ} and E_1^{β} typically change in different ways in the region of the first-order transition (Fig. 2). The half-width of the peak E_1^{β} changes smoothly, while that of the peak E_1^{γ} jumps discontinuously at the temperature of the $\gamma\rightarrow\beta$ transition. Such behavior could mean that the region occupied by the γ phase decreases in size as the temperature is raised, but the internal crystal structure in these

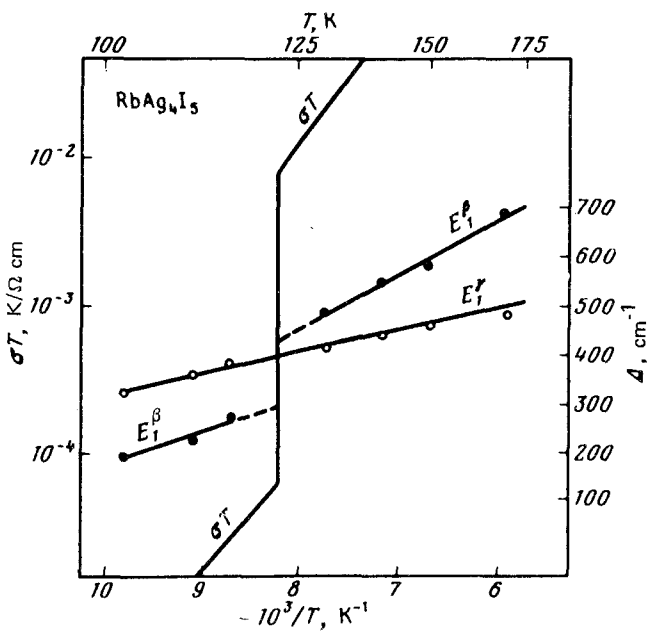

FIG. 2. The temperature dependence of the E_1^{γ} and E_1^{β} peaks in the modulational reflection spectrum. The curve for the temperature dependence of the ionic conductivity $\sigma T(T)$ of $RbAg_4I_5$ is taken from Funke (Ref. 7).

regions remains unchanged. The region occupied by the β phase would simultaneously increase. The effect on the excitons of the disordering in the β phase would come into play at the moment when the high ionic conductivity arose and the silver ions become mobile in the lattice. Figure 2 clearly shows the contribution of the thermal broadening and of the broadening due to the superionic disordering.

Analogous features corresponding to indirect excitonic absorption have been observed by the authors in the transmission and modulational reflection spectra of films of KAg_4I_5 and $NH_4Ag_4I_5$. In KAg_4I_5 at $T = 4.2$ K the peaks of the intense doublet in the modulational reflection spectrum are located at 3.343 and 3.327 eV, and in $NH_4Ag_4I_5$ at 4.2 K one observes a strong peak in the modulational reflection spectrum at 3.331 eV and a fainter structure at 3.308 eV.

The photoluminescence spectrum of $RbAg_4I_5$ at $T = 4.2$ K displays three broad emission peaks in the region in which luminescence had been detected previously[8]; the peaks occupy the positions 3.138, 3.061, and 3.002 eV against a continuous background with a short-wavelength cutoff of 3.245 eV.

[1)]Andreev *et al.* (Ref. 2) have suggested that this might be a first-order transition.

[2)]We do not rule out the possibility that the additional structure observed in the modulational reflection spectrum of the films is due to forbidden excitonic states which become more pronounced upon transition of the compound to the disordered phase.

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