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Secondary Emission of Doped Lithium Hydride Single Crystals

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Experimental studies of resonance Raman scattering (RRS) and of luminescence of excitons interacting with an impurity field and phonons in lithium hydride (LiH) crystals doped with Al, Mg, and Zn have been made. It has been shown that the presence of doped metal ions modifies the relaxation processes of excitons in the LiH lattice and gives rise to bound excitons with large and small radii.

1. Introduction

Lithium hydride is the simplest ionic crystal having the rock salt structure but its energy band structure is quite different from that of alkali halides possessing the same crystalline structure (*1, 2*). This difference between lithium hydride and alkali halide crystals determines many of its electron excitation and relaxation peculiarities.

At present it is well established that excitons in pure LiH crystals are free in the course of intraband relaxation and annihilate radiatively both without and with help of emission of one or more optical phonons (*3, 4*).

There is no direct experimental evidence for self-trapping of electron excitations during their relaxation in LiH crystals. Nevertheless, investigators (*5–10*) attribute broad bands with large Stoke shift, induced by band-to-band excitation, to the radiative annihilation of self-trapped excitons.

Substantial influence of impurities and intrinsic defects of the exciton relaxation processes is expected to take place because exciton–phonon interaction in lithium hydride crystals is rather weak (*3, 11*). Defects cause the decrease of free exciton luminescence and give rise to either bound excitons localized either by impurity-defect complexes (*12–14*) or, probably, by intrinsic defects (*15*).

In the present paper luminescence and resonance Raman scattering (RRS) of LiH doped with Al, Mg, and Zn are studied. The results show that impurity defects modify electron excitation relaxation in the lithium hydride lattice and give rise to localized exciton states with large and small radii.

2. Experimental

Single crystals of LiH were grown from the melt by the modified Bridgman–Stockbarger method using ultrasound (*16*). The samples used in this investigation were doped with Al, Mg, and Zn. The dopant content was about 0.03 wt%. The concen-

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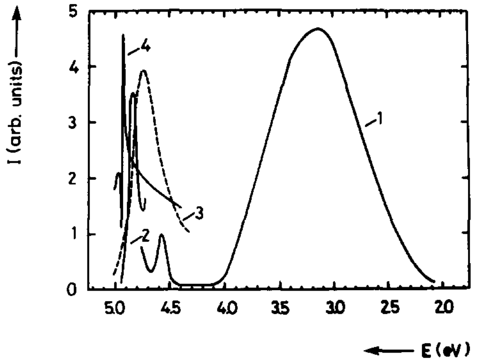

FIG. 1. Secondary emission (1); excitation of the secondary emission (2) (the 4.57-eV line); (3) (the band at 3.1 eV); and reflection (4) spectra (recorder curves) of LiH–Mg single crystals at 4.2 K.

tration of uncontrolled impurities in the samples was less than 10^{-3} wt%.

Secondary emission spectra at 4.2 K were recorded on the samples cleaved in liquid helium before measuring (*17*). The excitation source for luminescence and RRS at 4.2 K was a monochromatic beam of incident light obtained with the help of a double monochromator DMR-4 from the line spectrum of deuterium and mercury lamps. The secondary emission was also analyzed by a monochromator DMR-4.

A powerful high-pressure argon lamp, monochromators SF-4 and SPM-2 were used in our experiments at 77 K.

3. Results and Discussion

Figure 1 shows the secondary emission spectrum at 4.2 K of LiH–Mg crystals cleaved in liquid helium and excited in the region of the long-wavelength fundamental absorption edge. This emission spectrum consists of a narrow edge emission line at 4.57 eV and a broad low-energy band at 3.1 eV.

The maximum in the excitation spectrum of the 4.57-eV secondary emission line is at 4.84 eV. This energy is below the absorption energy of the $n = 1$ sec exciton by 0.11 eV (Fig. 1). The excited states responsible for the 4.57-eV secondary emission line are identified as those of excitons bound to defects in LiH–Mg crystals.

The maximum in the excitation spectrum of the 4.57-eV line is due to the resonance (zero-phonon) transition of the bound excitons and the binding energy of bound excitons is 0.11 eV.

The 4.57-eV line in the resonance excitation is caused by optical transitions with participation of the 2LO(Γ) phonons, since the energy separation between the maximum of the excitation spectrum and this line is 0.270 eV, which is equal to the energy of two LO(Γ) phonons in the LiH lattice at 4.2 K.

Optical processes giving rise to the resonance secondary emission line 4.57 eV are due to 2LO(Γ)-RRS and to 2LO(Γ)-phonon-assisted luminescence. This follows from the study of the spectral position of the edge emission line at different energies of the incident light E_L, illustrated in Fig. 2 in Raman-like representation.

The Raman shift E_L–E_S, where E_S is the emission energy, is constant when the energy of the incident light is below the resonance energy. It means that 2LO(Γ)-Raman scattering takes place. The 2LO(Γ)-Raman scattering efficiency increases when the in-

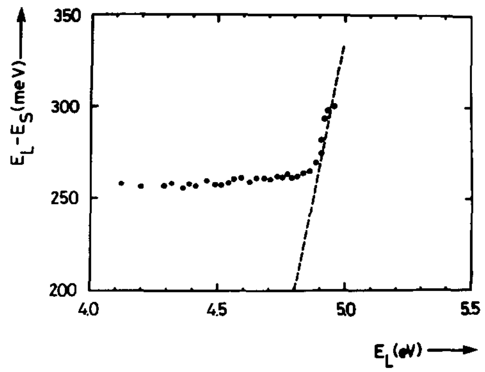

FIG. 2. Dependence of Raman shift for the secondary edge emission line on the incident light energy in LiH–Mg single crystals at 77 K.

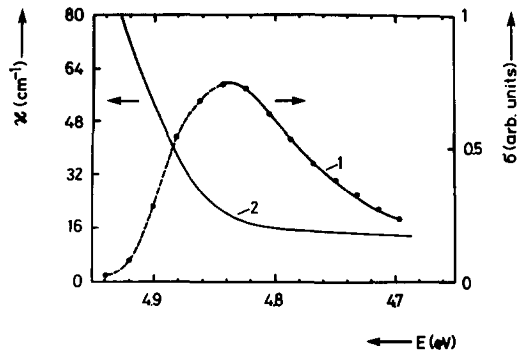

FIG. 3. Spectral dependence of the 2LO-Raman scattering efficiency (1) (solid line) and the absorption spectrum (2) of LiH–Mg single crystals at 77 K.

cident light energy is approaching the resonance transition energy (Fig. 3).

When the incident light energy is above the resonance energy, the edge emission line behaves like the 2LO(Γ)-phonon-assisted luminescence line, since the E_L–E_S plot has a slope equal to unity. Passing through the resonance absorption region of bound excitons, the RRS is gradually transformed into nonthermalized luminescence.

Bound excitons responsible for the 4.57-eV line have large radius, since the position of this line does not depend on the type of impurity in the crystal. This line was also observed in LiH crystals doped with Al and Zn (Fig. 4). (Secondary emission spectrum of LiH–Zn crystals is not shown in Fig. 4.)

The broad emission band at 3.1 eV is also associated with the exciton states disturbed by defects. The excitation spectrum of this band is shown in Fig. 1. The excitation spectrum of the 3.1-eV band is slightly shifted to the low-energy region relative to that of the 4.57-eV secondary emission line. One can probably explain this by overlap of the 3.1-eV band with another emission band associated with other localized electronic levels. We tentatively assume that an incident photon is absorbed by the same electron states that are common for both electron excitations, the radiative annihilation of which gives rise to the 4.57-eV line and the band at 3.1 eV.

The large Stokes shift and broad linewidth of the band at 3.1 eV indicate that the electron excitation responsible for this band is strongly localized. We suppose that the band at 3.1 eV is due to localized excitons, in other words, bound excitons with small radius.

The lifetime of the 3.1-eV band is a few tens of minutes at 4.2 K, which could be explained by a triplet nature of the relaxed bound exciton states with small radius.

Creation of bound excitons of both large and small radius, caused by the same defects in lithium hydride, resembles the coexistence of free and self-trapped excitons in alkali halides (*18, 19*). Bound excitons with small radius in doped lithium hydride crystals are analogous to the self-trapped excitons in pure crystals. In our case there is self-trapping for bound excitons with large radius due to the cooperation of the electron–phonon interaction and the defect potential. Such extrinsic self-trapping in crystals with a weak electron–phonon interaction was discussed by Toyozawa (*20*) and this idea has been used recently for an explanation of the experimental results in MgO–Ca crystals (*21*).

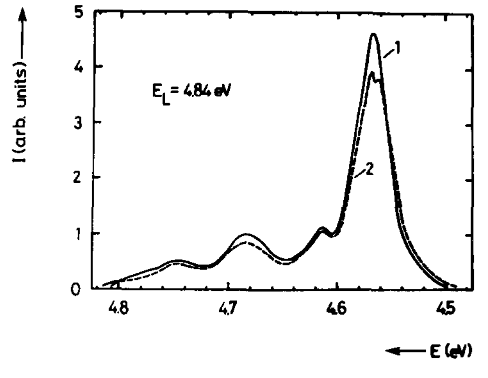

FIG. 4. Secondary emission spectra (recorder curves) of LiH–Al (1) and LiH–Mg (2) single crystals at 77 K and the resonance excitation.

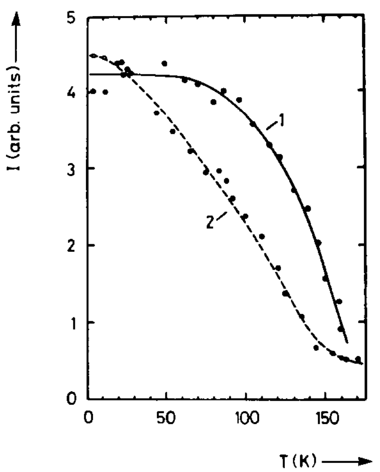

FIG. 5. Temperature dependences of the secondary emission of bound excitons with large radius (1) and small radius (2).

The temperature dependence of the luminescence of bound excitons with either large or small radius (Fig. 5) can be described by the formula

$$I(T) = \frac{I_0}{1 + C_1\exp(-E_1/kT) + C_2\exp(-E_2/kT)} .$$

The parameters used in fitting the data for bound excitons with large radius are $C_1 = 0.5 \pm 0.1$, $E_1 = 0.013 \pm 0.002$ eV, $C_2 = (3 \pm 2) \times 10^4$, and $E_2 = 0.12 \pm 0.01$ eV; for bound excitons with small radius are $C_1 = 2.4 \pm 0.2$, $E_1 = 0.012 \pm 0.002$ eV, $C_2 = (0.9 \pm 0.2) \times 10^3$, and $E_2 = 0.07 \pm 0.01$ eV.

The two activation energies indicate that there are two channels for nonradiative bound exciton recombination. The activation energy E_2 for bound excitons with large radius is close to the spectroscopically determined binding energy 0.11 eV. Thus, the nonradiative recombination process with the activation energy $E_2 = 0.12$ eV is their dissociation. The second nonradiative recombination process, with the activation energy $E_1 = 0.013$ eV, can be identified with the thermalization of bound excitons with large radius into the free exciton zone.

The activation energy $E_1 = 0.012$ eV for bound excitons with small radius may correspond to their thermalization into the zone of bound excitons with large radius and the activation energy $E_2 = 0.07$ eV corresponds to their dissociation.

The smaller energy value for thermal dissociation of a more tightly localized exciton state with a small radius in comparison with that of a bound exciton with a large radius can be explained, most likely, by the role of local vibrations of bound excitons with small radius.

On the basis of the temperature dependences of the bound exciton luminescence we suppose that the state of the bound exciton with small radius is separated from that of the bound exciton with large radius by a very small potential barrier.

Besides formation of the exciton states of bound excitons with large radius and small radius, the presence of impurities gives rise to local electron excitations which are created under the influence of direct optical excitation. Fig. 6 shows the spectral characteristics of the emission due to the impurity local states in the LiH–Mg crystals.

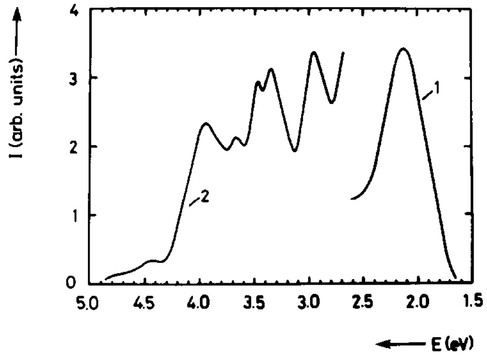

FIG. 6. Luminescence spectrum at the energy of excitation 2.95 eV (1) and luminescence excitation spectrum (2) (recorder curves) of the local centers associated with Mg ions at 77 K.

4. Conclusion

Secondary emission of LiH single crystals doped with metal impurities has been investigated. Our results can be interpreted in terms of the existence of bound excitons with large and small radii. Since bound excitons with large radius strongly interact with LO-phonons, one can see a very pronounced RRS. Cooperation of the defect potential and the lattice relaxation gives rise to the bound excitons with small radius. Dominant defects in lithium hydride crystals doped with metal ions are, probably, complexes formed by substitutional ions adjacent to lithium ion vacancies (*22–24*).

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