

Photostimulated processes in the Jahn-Teller system LiH(D):Ru

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 4055

(<http://iopscience.iop.org/0953-8984/4/15/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:48

Please note that [terms and conditions apply](#).

Photostimulated processes in the Jahn–Teller system LiH(D):Ru

G I Pilipenko†, A A Sabirzyanov†, D V Oparin†, V G Stepanov‡ and
F F Gavrilov†

† Department of Physics, Ural Polytechnical Institute, 620002 Ekaterinburg, Russia

‡ Department of Physics, Kazan State University, 420008 Kazan, Russia

Received 2 December 1991

Abstract. The optical absorption, luminescence and EPR methods have been used to study LiH(D) single crystals doped with Ru^{2+} . The formation of new absorption bands and EPR signal was observed after the illumination of crystals with light at $T = 77$ K. The possible model of photostimulated processes in LiH(D):Ru crystals is presented.

1. Introduction

In earlier work [1, 2] the observation of impurity centres in LiH and LiD crystals doped with some ions of 4d and 5d transition-metal series has been reported. In this paper, which is an extension of the previous work [3], the results of a study by optical spectroscopy and EPR of photostimulated processes in LiH(D) doped with Ru^{2+} (low-spin $4d^6$ configuration) are presented. Photostimulated processes in the LiH(D):Ru system have been interpreted in terms of the charge state change of impurity centres with tetragonal and cubic symmetry (the cubic centres exhibit a quasidynamical Jahn–Teller effect).

2. Experimental procedure

The LiH:Ru and LiD:Ru single crystals used in this work were grown by the Bridgman–Stockbarger method [4]. The ruthenium content in crystals as determined by spectral analysis was about 5×10^{-2} wt%.

The optical absorption measurements were made using a Specord M40 spectrophotometer with the sample kept under vacuum. The luminescence spectra were recorded with an SDL-2 spectrometer using an immersion nitrogen cryostat. The EPR measurements were performed on a Thomson THN-251 spectrometer operating at a frequency of 9.3 GHz with an Oxford Instruments variable-temperature accessory.

3. Results

The optical absorption spectra of LiH(D):Ru crystals are shown in figure 1. One can see three intense broad bands, labelled A, B and C, whose parameters are listed in

Table 1. Bands in the absorption spectra of LiH(D):Ru crystals ($T = 77$ K).

Band	ν (cm^{-1})		Isotopic shift (cm^{-1})
	LiH:Ru	LiD:Ru	
A	30000 ± 100	30400 ± 100	400 ± 200
B	24580 ± 20 and replicas with interval 400	24810 ± 20 and replicas with interval 290	230 ± 40
C	19750 ± 50	20050 ± 50	300 ± 100
D	20110 ± 20	20440 ± 20	330 ± 40
E	20360 ± 20 20840 ± 20	20600 ± 20 21060 ± 20 21540 ± 20	240 ± 40
G	12000 ± 1000	12000 ± 1000	

table 1. The crystals have a red or yellow colour depending on the relative intensities of these bands which vary from sample to sample. This indicates that absorption bands A, B and C are likely to be due to different impurity defects.

To estimate the oscillator strength of transitions associated with the absorption bands of LiH(D):Ru crystals the Smakula equation may be used [5]. The overlap of bands A and B hinders exact determination of their shape and width, whereas for band C this can be done easily. If we take the index n of refraction as 1.984 [6], the absorption coefficient K_{max} at the band maximum as 30 cm^{-1} , the full width W of the band at half-maximum as 0.35 eV and the concentration N of colour centres as $2.3 \times 10^{18} \text{ cm}^{-3}$, we obtain the oscillator strength f for band C as approximately 0.02. This value can also be regarded as a rough estimate of the oscillator strengths of bands A and B, since they have similar values of K_{max} and W .

At a temperature of 77 K, band B exhibits a series of narrow equidistant lines separated by intervals of 400 and 290 cm^{-1} in LiH:Ru and LiD:Ru, respectively. The energy of the first peak is given in table 1 as the energy of band B. The ratio of these intervals, being equal to 1.38, is close to $\sqrt{m_{\text{D}}/m_{\text{H}}} = 1.41$, where m_{D} and m_{H} are the masses of deuterium and hydrogen, respectively. This suggests that the observed structure is due to the local mode of impurity defect, which involves predominantly the H⁻ (D⁻) ions in the nearest neighbourhood of the ruthenium ion.

Heating to 300 K leads to a red shift of bands A and C, while band C decreases in intensity. Band B is not shifted, and the vibrational structure of this band disappears.

Bands A, B and C are stable towards heating up to 450 K and towards electrolytic colouration. However, illumination of the crystals at $T = 77$ K with light of frequency corresponding to band C gives rise to photochromic transformations including the destruction of band C and the formation of new bands D, E and G (table 1 and figure 2). The intensity of band A is reduced slightly in this case while that of band B remains unaffected.

The photo-induced band E consists of at least two lines separated by intervals of 480 cm^{-1} for both LiH:Ru and LiD:Ru (figure 2). The structure of band E may be due to the excitation of the local mode in which lithium or ruthenium ions participate. The photo-induced absorption bands D, E and G are most efficiently bleached with light of

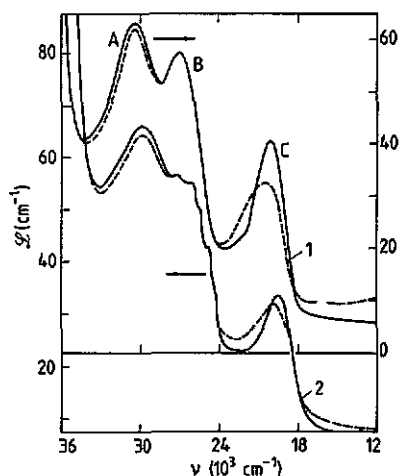


Figure 1. Optical absorption spectra of LiD:Ru (curve 1) and LiH:Ru (curve 2) crystals measured at $T = 77$ K: —, initial spectrum; ---, after illumination with band-C light at $T = 77$ K for 1 min.

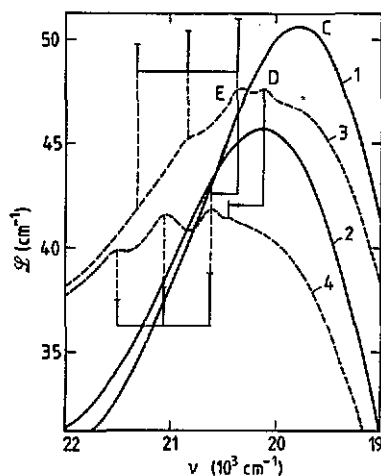


Figure 2. Bands C, D and E in the absorption spectra measured at $T = 77$ K for LiH:Ru (curves 1 and 3) and for LiD:Ru (curves 2 and 4): —, initial spectrum; ---, after illumination with band-C light at $T = 77$ K for 1 min.

frequency corresponding to band G ($11\,000$ – $14\,000$ cm^{-1}), whereas the intensity of band C increases. However, the intensity of band C is not restored to the original value existing before illumination with light of frequency corresponding to band C.

The heating of crystals of LiH(D) : Ru exposed to band-C light up to room temperature completely restores the original absorption spectrum.

The above-mentioned transformations of the LiH(D) : Ru absorption spectrum indicate that photochromic processes due to the charge exchange occur in the crystals.

Upon the excitation with light of frequency corresponding to absorption band B, luminescence is observed whose spectrum consists of a series of replicas of the zero-phonon line separated by intervals of 1600 cm^{-1} in LiH:Ru and 1140 cm^{-1} in LiD:Ru, thus determining the local mode frequency (figure 3). The first lines in the series corresponding to the pure electronic line are located at $20\,680$ cm^{-1} and $20\,900$ cm^{-1} in LiH:Ru and LiD:Ru, respectively. The zero-phonon lines are accompanied by phonon sidebands which have a resolved structure at $T = 77$ K. The local mode frequency is beyond the lattice vibrational spectrum and lies within the range 1600 – 2200 cm^{-1} reported in [7] as characteristic of the metal–hydrogen stretching vibration in hydride complexes.

The luminescence excitation spectrum is identical with band B in the absorption spectrum. The vibrational structure of band B is due to the excitation of the local modes interpreted as deformation modes.

To study the nature of impurity defects and the corresponding absorption bands, the EPR technique has been employed. The absorption spectrum with the three bands A, B and C is observed in as-grown crystals, and no EPR signal can be detected. The illumination with the band-C light at 4.2 – 77 K gives rise to the formation of paramagnetic centres of two species, denoted by Ru(IT) (figure 4) and Ru(A) (figure 5). Ru(IT) centres are observed between 4.2 and 100 K, and Ru(A) centres between 30 and 110 K.

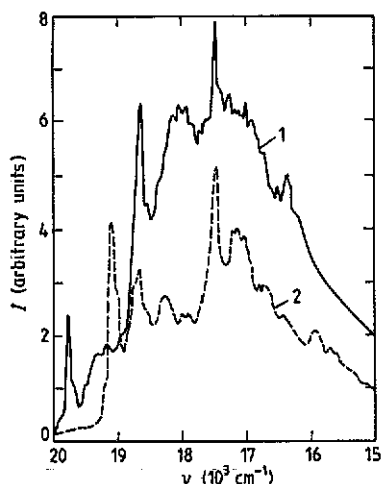


Figure 3. The recorded luminescence spectra of LiD:Ru (curve 1) and LiH:Ru (curve 2) at $T = 77$ K under excitation with $\lambda = 400$ nm.

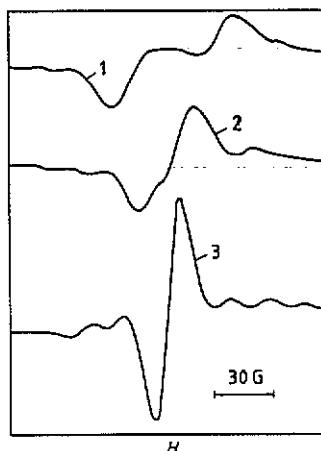


Figure 4. EPR spectra of Ru(JT) centres in LiH:Ru crystals measured at $T = 4.2$ K after illumination with band-C light at $T = 77$ K: curve 1, $H \parallel [100]$; curve 2, $H \parallel [110]$; curve 3, $H \parallel [111]$.

The EPR spectrum of Ru(JT) centres at $T = 4.2$ K consists of two lines which coalesce to form an intense symmetric line (figure 4, curve 3) at the applied magnetic field orientation $H \parallel [111]$. The anisotropic EPR spectrum of Ru(JT) centres consisting of two lines undergoes transformation to a single isotropic line in the temperature range 20–30 K.

The analysis of EPR spectra of Ru(JT) centres permits one to present them as Ru^{+} ions in cation sites in the LiH(D) lattice, exhibiting the quasidynamical Jahn–Teller effect. Ru^{+} ions have a $4d^7$ external electron shell influenced by the strong crystal field of octahedrally coordinated H^{-} (D^{-}) ligands. The low-spin electronic configuration of the Ru^{+} ground state is $(t_{2g})^6 e_g ({}^2E_g \text{ term})$.

The EPR spectrum of Ru(JT) centres is well described by the three-state effective Hamiltonian [8] regarding random-strain, Zeeman and hyperfine coupling. The measured parameters of the effective Hamiltonian for Ru(JT) centres are [3] $g_{\perp} = 2.050$, $g_{\parallel} = 0.013$ and $A = 22 \times 10^{-4} \text{ cm}^{-1}$.

The EPR spectrum of the Ru(A) centres is described by the axially symmetric spin Hamiltonian with an effective electron spin $S = \frac{1}{2}$ and nucleus spin $I = \frac{5}{2}$. The parameters of this spin Hamiltonian are [3] $g_{\perp} = 2.177$, $g_{\parallel} = 1.995$, $A_{\perp} = 21.3 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\parallel} = -9.8 \times 10^{-4} \text{ cm}^{-1}$.

The Ru(A) centres presumably consist of Ru^{+} ions (low-spin $4d^7$ configuration) in cation sites in the close vicinity of lattice defects which reduce the Ru^{+} ion local symmetry to tetragonal.

4. Discussion

As shown by the EPR, the exposure of LiH(D):Ru crystals to light produces Ru^{+} ions. Some of these occupy the cation sites with pure octahedral symmetry, and the others

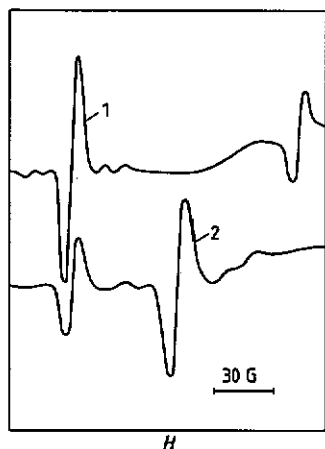


Figure 5. EPR spectra of Ru(A) centres in LiD:Ru crystals measured at $T = 110$ K after illumination with band-C light at $T = 77$ K: curve 1, $H \parallel [100]$; curve 2, $H \parallel [110]$.

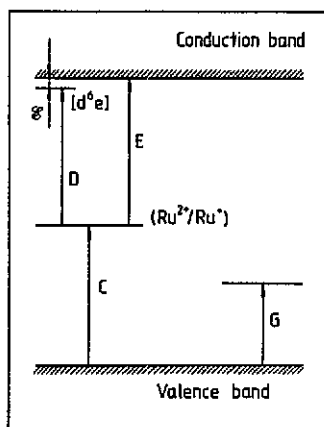


Figure 6. Energy diagram of electronic transitions associated with the photostimulated processes in LiH(D):Ru crystals.

appear in the close vicinity of the lattice defect (cation or anion vacancy, etc) which lowers the local symmetry of the impurity to tetragonal.

The unparamagnetic state of ruthenium ions can be identified with the charge state Ru^{2+} (low-spin $4d^6$ configuration with closed $(t_2)^6$ shell).

Since no EPR signal is detected in LiH(D):Ru crystals before illumination, bands A, B and C in the optical absorption spectrum should be associated with the presence of Ru^{2+} ions. The oscillator strength f of these bands indicates that the absorption cannot arise from the intra-configurational d-d transitions which have f of the order of 10^{-4} . Bands A, B and C can be attributed rather to the charge-transfer transitions whose oscillator strength f is 10^{-2} –1. Band C, in particular, can be attributed to the electron transfer from the H^- (D^-) ion to the Ru^{2+} ion.

The energy of the ligand-metal charge-transfer (LMCT) transition for band C can be calculated from the equation [9]

$$h\nu = I(L^-) - I(M^+) + \delta(M^{2+}) - \delta(M^+) + \gamma \quad (1)$$

where I are the ionization potentials (IPs), $\delta(M^{2+})$ and $\delta(M^+)$ are the crystal-field stabilization energies (CFSEs) of the initial and final transition states, respectively, and γ is a constant parameter for a given host. The IPs of the H^- and Ru^+ free ions are 0.75 eV and 16.76 eV, respectively [10]. The CFSEs of the initial d^6 (Ru^{2+}) and final d^7 (Ru^+) configurations are $24Dq$ and $18Dq$, respectively, the Dq value in LiH(D) being about 0.25 eV. The parameter γ can be regarded as empirical; its value should be 17.0 eV to fit the calculated value of the band-C transition energy with its experimental value. A rough estimate of γ may be obtained on the basis of the simple transfer model in a manner similar to the derivation of the Hilsch-Pohl formula for excitons [11]:

$$\gamma = (2\alpha_M - 1)e^2/r_0 \quad (2)$$

where α_M and r_0 are the Madelung constant and corresponding lattice distance, respectively. Equation (2) gives $\gamma = 17.6$ eV for LiH:Ru.

Bands D and E are due to ruthenium ions in the Ru^+ charge state. They cannot be identified with the LMCT transitions (the electron transfer from a neighbouring H^- ion to an Ru^+ ion, forming Ru^0). The difference between the first and second IPs of ruthenium is 9.4 eV. Because of this, the calculation of the transfer energy from H^- (D^-) to Ru^+ by equation (1) gives a value which far exceeds the experimental position of band D and E maxima.

Absorption band D may be explained in terms of the 'donor' exciton, whose hole component is localized at the Ru^+ ion, charging it positively relative to the lattice, and the electron is bound by the Coulomb field of this charge. In this way the electronic transition associated with band D is described by the reaction



the square brackets denoting the Coulomb coupling of electron with the Ru^{2+} ion (figure 6).

In view of the fact that band C arises from the electronic transition from the valence band to the Ru^{2+} ion level, the sum of energies of bands C and D corresponds to the electronic transition from the valence band to the 'donor' exciton state. Adding $h\nu(\text{C}) + h\nu(\text{D})$ gives 4.94 eV for LiH:Ru and 5.02 eV for LiD:Ru which is very close to the first exciton peak position in the pure LiH and LiD crystals (4.94 eV and 5.04 eV at $T = 80$ K) [12]. The described picture of the electronic transition is illustrated in figure 6.

The first peak of band E can be assigned to the photo-induced transition involving the excitation of an electron from the Ru^+ ion to the conduction band. The sums of energies $h\nu(\text{C}) + h\nu(\text{E})$ are 4.97 eV and 5.04 eV for LiH:Ru and LiD:Ru, respectively, which is in good agreement with the forbidden gap energies for LiH and LiD (4.98 eV and 5.09 eV at $T = 80$ K) [12] (figure 6). The 'donor' exciton binding energy ϵ , as evaluated from a comparison of the positions of bands D and E, is about 200 cm^{-1} (0.02 eV).

Absorption band G can be assigned to the hole centres formed by hole capture at traps in the crystal.

By means of the charge transfer, Ru^{2+} converts to Ru^+ with the subsequent migration of a hole into the valence band and its capture at a trap. We believe that this process accounts for the formation of the Jahn–Teller $\text{Ru}(\text{JT})$ centres.

The formation of Ru^+ paramagnetic centres of tetragonal symmetry ($\text{Ru}(\text{A})$ centres) can be understood by assuming the existence of impurity centres composed of a substitutional Ru^{2+} ion and the lattice defect which provides charge compensation and tetragonal local symmetry.

The nature of the defects responsible for bands A and B is not clear at present.

5. Conclusion

Three intense absorption bands have been detected in LiH(D):Ru crystals. They were ascribed to impurity Ru^{2+} centres and interpreted as due to the charge-transfer transitions. The excitation with band-C light at $T = 77$ K leads to the formation of new absorption bands along with an EPR signal of two paramagnetic centres attributed to Ru^+ ions in a low-spin $4d^7$ configuration. The new absorption bands and EPR signal can be destroyed by near-infrared illumination at 77 K or by heating to 300 K.

The proposed explanation of reversible photostimulated processes in $\text{LiH(D)} : \text{Ru}$ crystals implies that upon the illumination with band-C light the electron transfer from nearby H^- (D^-) anion to the Ru^{2+} ion takes place.

The photo-induced bands D and E were ascribed to the 'donor' exciton and photoionization state, respectively.

References

- [1] Sabirzyanov A A, Oparin D V, Pilipenko G I and Gavrilov F F 1989 *Abstracts 7th All-Union Conf. on Radiation Physics and Chemistry of Inorganic Materials* (Riga: Latvian Academy of Science) p 497 (in Russian)
- [2] Pilipenko G I, Stepanov V G, Sabirzyanov A A, Oparin D V and Gavrilov F F 1990 *Abstracts 9th Jubilee Scientific and Practical Conf. of Ural Polytechnical Institute (Physico-Technical Department Section)* (Sverdlovsk: Ural Polytechnical Institute) p 49 (in Russian)
- [3] Pilipenko G I, Sabirzyanov A A, Stepanov V G, Oparin D V, Izotov V V and Gavrilov F F 1992 *J. Phys.: Condens. Matter* **4** 4047
- [4] Sabirzyanov A A, Oparin D V, Pilipenko G I and Gavrilov F F 1990 *Mineralogical Crystallography, Crystallogeneses, Crystallosynthesis* ed N P Yushkin and A M Askhabov (Syktyvkar: Akademii Nauk Ukrainskoi SSR) p 105 (in Russian)
- [5] Fowler W B 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic) p 53
- [6] Staritzky E and Walker D I 1956 *Anal. Chem.* **28** 1055
- [7] Mackay K M 1966 *Hydrogen Compounds of the Metallic Elements* (London: E & FN Spon)
- [8] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
- [9] Eremin M V 1978 *Spectroscopy of Crystals* ed P P Feofilov (Leningrad: Nauka) p 39 (in Russian)
- [10] Moore C E 1970 *US Clearinghouse Federal Scientific and Technical Information, P B Report 194773*
- [11] Mott N F and Gurney R W 1948 *Electronic Processes in Ionic Crystals* (Oxford: Clarendon)
- [12] Plekhanov V G, Pustovarov V A, O'Connell-Bronin A A, Betenekova T A and Cholakh S O 1976 *Fiz. Tverd. Tela* **18** 2438 (in Russian)