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Quasidynamical Jahn–Teller effect in the electron paramagnetic resonance spectra of Ru⁺ ions in lithium hydride and deuteride

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

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

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

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Abstract. The formation of two independent paramagnetic centres Ru(π) and Ru(A) was detected by the EPR method in LiH and LiD single crystals doped with ruthenium, after illumination with visible light at $T = 77$ K. Both centres were assigned to Ru⁺ with low-spin $4d^7$ configuration. Ru(π) centres exhibit a quasidynamical Jahn–Teller effect. The values of tunnelling splitting 3Γ and random-strain splitting δ were estimated to be 24 cm^{-1} and 6.0 cm^{-1} , respectively. The Ru(A) centre was found to have tetragonal symmetry, with the unpaired electron in a $4d_{3z^2-r^2}$ orbital.

1. Introduction

Lithium hydride is a perfect host for studying metal–hydrogen chemical bonding of transition-metal paramagnetic impurities. However, few paramagnetic ions (Ni⁺ and Ni²⁺ [1], Mn²⁺ [2, 3] and Rh²⁺ [4]) have been able to be incorporated into LiH host to date, because most transition metals are insoluble in the LiH melt.

Some transition metals of the 4d and 5d groups are promising as dopants in the LiH host. Thus, the comprehensive analysis of two paramagnetic rhodium centres in LiH and LiD crystals has been reported in [4]. This provided an impetus for searching for other 4d and 5d transition metals capable of reacting with lithium hydride. In the course of experiments, LiH(D) crystals doped with Ru, Rh, Pd and Ir were obtained, as was verified by optical absorption and EPR [5–10].

In the present paper the results of EPR studies on LiH:Ru and LiD:Ru crystals are presented. The Jahn–Teller effect was observed for the first time in ruthenium ions in a cubic host, surrounded by hydride ions.

2. Experimental procedure

The LiH and LiD compounds possess the rock-salt crystal structure; the lattice parameters are 4.084 \AA and 4.068 \AA , respectively. LiH:Ru and LiD:Ru single crystals were grown by the Bridgman–Stockbarger method [8]. The ruthenium content in crystals was about 5×10^{-2} wt%. The crystals obtained had a red colour because of the presence of ruthenium.

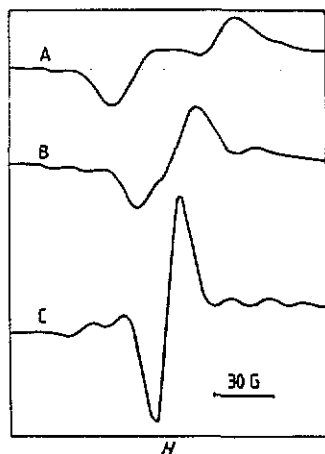


Figure 1. The EPR spectra of Ru(JT) centres in LiH:Ru at $T = 4.2$ K after illumination with light from a DRK-120 lamp; curve A, $H \parallel [100]$; curve B, $H \parallel [110]$; curve C, $H \parallel [111]$.

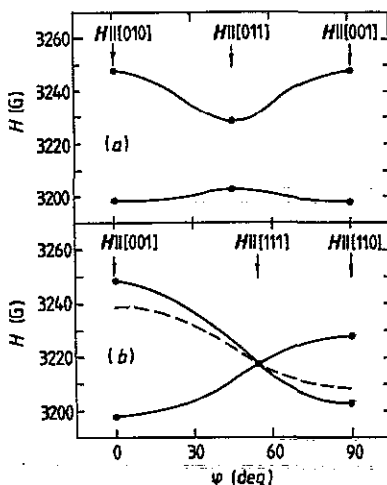


Figure 2. The angular dependence of the EPR spectra of Ru(JT) centres in LiH:Ru for magnetic field rotation in (a) the (100) plane and (b) the (110) plane: —, experimental curves; ---, theoretical angular dependence of the high-field EPR line (for H orientations with $1 \geq n \geq 1/\sqrt{3}$) in the case of the pure dynamic Jahn-Teller effect, as calculated using equation (1). The analogous theoretical curve for the low-field EPR line coincides with appropriate experimental curve.

The EPR measurements were performed on an X-band Thomson THN-251 spectrometer, operating at a frequency of 9.3 GHz. An Oxford Instruments variable-temperature accessory was employed for temperature control.

3. Results

The paramagnetic centres of two species, both associated with ruthenium ions, were detected in LiH:Ru and Li:Ru crystals after illumination with visible light at a temperature of 77 K.

One species, denoted as Ru(JT), is observed between 4.2 and 100 K. The other species, denoted as Ru(A), is detected between 30 and 110 K. At a temperature of 4.2 K the EPR signal intensities of these centres are low.

The low-temperature EPR spectrum of Ru(JT) centres is given in figure 1. It consists of two lines with an asymmetric shape characteristic of 'powder-pattern-like' lines. Such a lineshape might indicate the presence of inhomogeneous broadening due to the random distribution of host lattice imperfections in the environment of paramagnetic centres.

The low-temperature EPR spectrum of Ru(JT) centres is anisotropic; its angular dependence for an applied magnetic field orientation relative to the crystallographic axes of the host lattice in (100) and (110) planes is shown in figure 2. The position of lines represented by the full circles in figure 2 was found as the positions of peak maxima obtained by the decomposition of the integral EPR absorption line into the sum of two Gaussian peaks. The largest separation of the two lines in the low-temperature spectrum occurs for a magnetic field orientation along one of the fourfold axes. When the magnetic

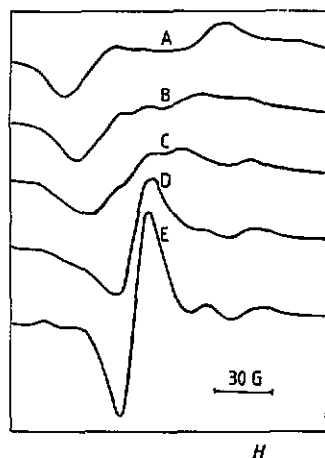


Figure 3. The temperature transformation of the EPR spectra of Ru(II) centres in LiD:Ru: curve A, 4.0 K; curve B, 8.0 K; curve C, 12.5 K; curve D, 20.5 K; curve E, 29.7 K. The magnetic field orientation $H \parallel [100]$.

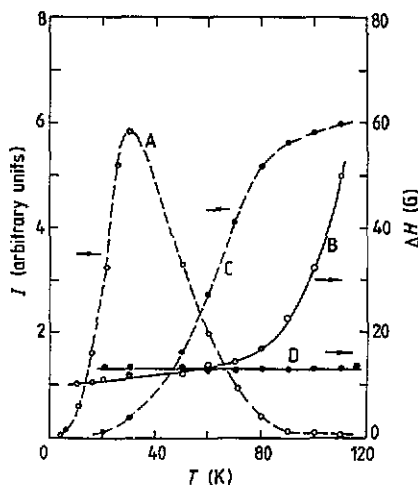


Figure 4. The temperature dependence of the intensities and linewidths of the isotropic EPR spectrum of Ru(II) centres (curves A and B) and the axial EPR spectrum of Ru(A) centres (curves C and D) in LiD:Ru.

field is oriented parallel to a [111] crystallographic direction, the two lines coalesce, and a single intense symmetric line corresponding to $g = 2.051$ is observed (figure 1, curve C). The symmetric lineshape at $H \parallel [111]$ indicates that physical factors responsible for inhomogeneous line broadening at other orientations are averaged.

At the orientation $H \parallel [111]$ the hyperfine structure (HFS) of the Ru(II) EPR spectrum is resolved. It consists of six lines with low intensities which are symmetrically located about the central intensive line. The HFS is due to the interaction of the unpaired electron of the Ru(II) centre with the nucleus spins $I = \frac{5}{2}$ of the odd ^{99}Ru (abundance 12.7%) and ^{101}Ru (abundance 17.0%) isotopes whose magnetic moments are approximately equal. The measured value of the HFS constant A_{111} at the orientation $H \parallel [111]$ is equal to $21.3 \times 10^{-4} \text{ cm}^{-1}$. The central intensive line is appropriate for even Ru isotopes (abundance 70.3%) with nucleus spin $I = 0$.

The presence of HFS in the Ru(II) spectrum is evidence that ruthenium ions in a paramagnetic state are responsible for this centre. As will be shown below, the oxidation state of ruthenium ions is Ru⁺ with a low-spin $4d^7$ electron configuration.

Significant changes in the EPR spectra are produced on increase in the temperature; the anisotropic spectrum intensity decreases and the isotropic spectrum arises which consists of a single symmetric line. Temperature transformation from an anisotropic low-temperature Ru(II) spectrum to a new isotropic spectrum with a g -value identical with the g -value of the low-temperature spectral line at the orientation $H \parallel [111]$ is shown in figure 3. The temperature dependence of new isotropic Ru(II) spectrum intensity is presented in figure 4. The decrease in the isotropic line intensity with temperature increase above 30 K is probably due to spin-lattice relaxation processes, as confirmed by the linewidth broadening (figure 4, curve B).

The EPR spectrum of Ru(A) centres is presented in figure 5. At a temperature of 110 K the pure Ru(A) spectrum can be seen without interference from Ru(II) centres. The angular dependence of the Ru(A) spectrum when the external magnetic field is oriented in a (100) plane is given in figure 6. Figure 4 shows the temperature dependences

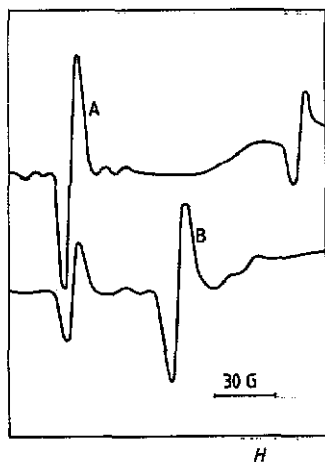


Figure 5. The EPR spectra of Ru(A) centres in LiD:Ru at $T = 110$ K: curve A, $H \parallel [100]$; curve B, $H \parallel [110]$.

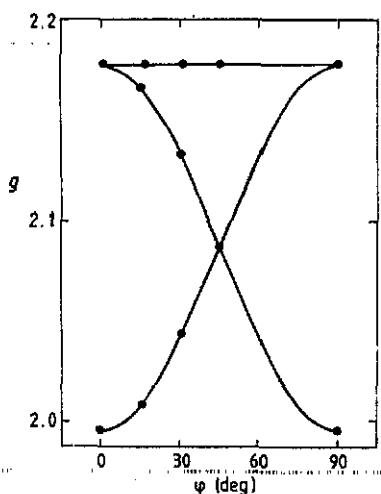


Figure 6. The angular dependence of the EPR spectrum of Ru(A) centres in LiD:Ru: ●, experimental data; —, angular dependence calculated using the formulae for axial symmetry.

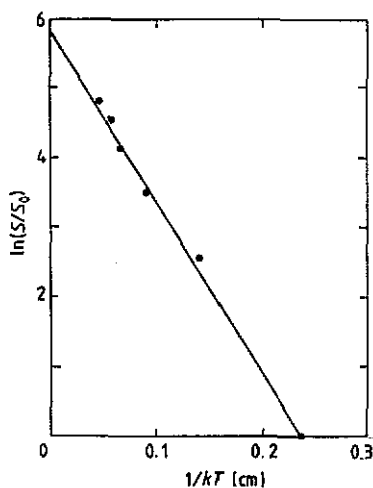


Figure 7. The dependence of $\ln(S/S_0)$ on the value of $1/kT$.

of the intensity and linewidth of the Ru(A) centres. The observed spectrum results from superposition of three magnetically inequivalent axially symmetric centres whose principal symmetry axes lie along the crystallographic fourfold axes. Ru(A) centres are also associated with Ru^+ (low-spin $4d^7$ configuration), as is evident from the HFS produced by the interaction with nucleus spin $I = \frac{7}{2}$ of odd Ru isotopes. An examination of temperature dependence of the Ru(A) spectrum shows the spectrum shape and its anisotropy to remain unchanged. Only the lines intensity vary with temperature (figure 4).

Heating the crystals to room temperature or illumination with light of a wavelength more than 700 nm at 77 K were found to result in the disappearance of both the Ru(π) and the Ru(A) EPR signals.

From the comparison of the EPR spectra of the Ru(π) and Ru(A) centres in LiH:Ru and LiD:Ru the linewidth for both centres in LiH:Ru was found to be approximately

twice that in $\text{LiD} : \text{Ru}$. This is due to the superhyperfine interaction with the hydrogen nuclei, which for the deuterium nuclei is negligible.

4. Discussion

The following features of the anisotropic low-temperature Ru(JT) EPR spectrum are notable:

- (i) the presence of two asymmetric lines characteristic of 'powder-pattern-like' lines;
- (ii) nearly symmetric position of spectral lines about the magnetic field value corresponding to the line position at the orientation $\mathbf{H} \parallel [111]$;
- (iii) coalescence of asymmetric spectral lines at the orientation $\mathbf{H} \parallel [111]$, giving a single intensive line with symmetric shape which means that the inhomogeneities are averaged at this orientation;
- (iv) transformation from anisotropic spectrum consisting of two lines to a single isotropic line, as the temperature rises.

These features are characteristic of a limiting dynamic case of the Jahn–Teller effect in EPR spectra of systems with a ${}^2\text{E}$ orbital ground state [11–13].

This can lead to the conclusion that the Ru(JT) centre represents a Ru^+ ion located in a cation site of the LiH or LiD lattice. Ru^+ ions have a $4d^7$ external electron shell which is influenced by a strong crystal field of octahedrally coordinated H^- ligands. The low-spin electronic configuration of the ground state of Ru^+ is $(t_{2g})^6 e_g$.

Coupling between the ground ${}^2\text{E}$ orbital state and the vibrational modes of the cluster formed by the Ru^+ ion and its nearest neighbours via Jahn–Teller linear coupling and non-linear interactions results in a vibronic energy-level structure characterized by a ${}^2\text{E}$ vibronic ground state and excited vibronic A_1 and A_2 singlet levels. Accidental degeneracy of A_1 and A_2 levels is removed by non-linear interactions [12, 14]; the energy separation between the lowest vibronic A_1 (or A_2) singlet and the ${}^2\text{E}$ vibronic ground state is designated as the tunnelling splitting 3Γ .

The vibronic ground doublet is very sensitive to the presence of random strains in the crystal and its degeneracy is removed by the random-strain coupling [12, 14].

The three-state (the vibronic ground doublet and the nearest vibronic singlet) effective Hamiltonian can be applied to describe Ru^+ (Ru(JT) centres) EPR spectrum in the presence of the vibronic, random-strain and Zeeman interactions [12, 14, 15].

In the formalism of the three-state effective Hamiltonian it has been shown that the character of the EPR spectrum of systems with a vibronic ${}^2\text{E}$ state depends on the value of the ratio $\delta/3\Gamma$, where δ is an average random-strain splitting of the vibronic doublet.

The features of the EPR spectrum of Ru(JT) centres noted above are typical of the low-temperature dynamical Jahn–Teller effect in the case when the tunnelling splitting is sufficiently large relative to the random strain and Zeeman splitting. It is the latter two which determine the EPR spectrum shape in the present case.

Using the three-state effective Hamiltonian gives the following first-order expression for EPR transitions [12]:

$$h\nu_{\pm} = \{g_1 \pm \frac{1}{2}qg_2[(3n^2 - 1) \cos \varphi + \sqrt{3}(l^2 - m^2) \sin \varphi]\} \beta H + A_1 M_I \quad (1)$$

where the \pm subscript differentiates the solutions for the two Kramers doublets ψ_+ and ψ_- ; l , m and n are the direction cosines of the applied magnetic field relative to the cubic fourfold axes; M_I is the nuclear spin projection quantum number; A_1 is the hyperfine

interaction constant; φ is the angle varying from 0 to 2π which represents the distribution of random-strain components from site to site in the crystal. It is the random distribution of φ that causes the asymmetric lineshape of the EPR transitions, similar to that of a powder spectrum.

The fitting of the experimental angular dependence of the Ru(III) EPR spectrum to the theoretical dependence (1) is shown in figure 2. If $g_1 = 2.050$ and $qg_2 = 0.013$, the low-field line (for H orientations with $1 \geq n \geq 1/\sqrt{3}$) is well described by the theoretical dependence. The high-field line (for H orientations with $1 \geq n \geq 1/\sqrt{3}$) is shifted to higher magnetic fields. This means that the state associated with the high-field EPR line (for H orientations with $1 \geq n \geq 1/\sqrt{3}$) is mixed with the nearest excited vibronic singlet.

Using the result of the numerical solution of the effective Hamiltonian performed for various relative magnitudes of tunnelling splitting 3Γ , strain splitting δ and Zeeman splitting the excited vibronic singlet (either A_1 or A_2) which is mixed with one of the vibronic 2E -state Kramers doublets can be identified as well as the value of ratio $\delta/3\Gamma$ which determines the type of Jahn-Teller effect [11-13].

Since qg_2 is positive for the Ru^+ ion with the $4d^7$ electron configuration, the selective shift of the high-field spectral component (for H orientations with $1 \geq n \geq 1/\sqrt{3}$) to higher magnetic fields identifies the nearest excited state to be the A_1 vibronic singlet. Then, by comparing the experimental angular dependence of the high-field line, whose anisotropy is due to the coupling to an excited vibronic singlet A_1 , with the calculated angular dependences presented in [12] we obtain the ratio $\delta/3\Gamma = 0.25$.

The low-temperature spectra of Ru(III) centres characterized by the quasidynamical Jahn-Teller effect are reliably detected in lithium hydride and deuteride single crystals from different crystal growth procedures which indicates the crystal structure of samples to be well reproduced. The average magnitude of the random strains in crystals can be deduced from the value of $\delta/3\Gamma$, if the value of the tunnelling splitting is known.

The value of 3Γ can be estimated from the temperature dependence of the isotropic spectrum intensity. The isotropic spectra of pure dynamic and quasidynamic Jahn-Teller systems arising with increasing temperature can result either from the thermal population of the nearest excited vibronic singlet or from increasing the relaxation rate within a split 2E vibronic doublet.

If we suppose that for the LiH(D):Ru system the excited vibronic singlet A_1 is sufficiently close to the ground 2E vibronic level as follows from the selective shift of one spectral component and rapid increase in the isotropic spectrum intensity between 4.2 and 30 K (figure 4, curve A), it is reasonable to assume that the thermal population of the A_1 level is responsible for the isotropic spectrum. Using this assumption the temperature dependence of the isotropic spectrum intensity can be described by the following expression:

$$S \sim S_0 \exp(-3\Gamma/kT). \quad (2)$$

The $\ln(S/S_0)$ dependence on $1/kT$ is given in figure 7, showing equation (2) to describe satisfactorily the temperature variation in the isotropic spectrum intensity. The value of 3Γ was calculated to be 24 cm^{-1} . This value together with the previously determined ratio $\delta/3\Gamma$ fixes the value of the average random-strain splitting δ as 6.0 cm^{-1} . Since it was not possible to determine accurately what fraction of the isotropic spectrum might be due to averaging by relaxation, the values of 3Γ and δ must be regarded as an approximate result.

The Ru(A) EPR spectrum is described by the spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (3)$$

with effective electron spin $S = \frac{1}{2}$ and nucleus spin $I = \frac{5}{2}$ for odd ${}^{99}\text{Ru}$ and ${}^{101}\text{Ru}$ isotopes.

The spin-Hamiltonian parameters are

$$\begin{aligned} g_{\perp} &= 2.177 & g_{\parallel} &= 1.995 \\ A_{\perp} &= 21.3 \times 10^{-4} \text{ cm}^{-1} & A_{\parallel} &= -9.8 \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

The principal symmetry axes of the \mathbf{g} -tensor and the \mathbf{A} -tensor of ruthenium nuclei hyperfine interaction coincide and are parallel to the [100], [010] and [001] crystallographic directions.

We believe the Ru(A) centres to be associated with Ru^+ ions (low-spin $4d^7$ configuration) which occupy cation sites in the neighbourhood of lattice defects, thus reducing the Ru^+ local symmetry to tetragonal. This leads to the Ru^+ ground 2E_g -state splitting into two orbital singlets ${}^2A_{1g}$ ($4d_{3z^2-r^2}$) and ${}^2B_{1g}$ ($4d_{x^2-y^2}$). The unpaired electron is certain to occupy the ${}^2A_{1g}$ ($4d_{3z^2-r^2}$) orbital, since the \mathbf{g} -tensor components satisfy the condition $g_{\perp} > g_{\parallel}$ which is appropriate to the octahedral coordination with static extension along the z axis.

5. Conclusion

In the present work, LiH and LiD single crystals doped with ruthenium were obtained and investigated by the EPR method for the first time. No EPR signal could be detected in as-grown samples. The EPR spectra of two paramagnetic centres Ru(T) and Ru(A) associated with Ru^+ ions with low-spin $4d^7$ configuration were observed in crystals after exposure to visible light at $T = 77$ K.

At liquid-helium temperature the EPR spectrum of the Ru(T) centres was anisotropic and consisted of two asymmetric lines. With increasing temperature to 25–30 K the anisotropic spectrum underwent transformation to an isotropic spectrum consisting of a single symmetric line. Such a behaviour of EPR spectrum is attributed to the quasidynamical Jahn–Teller effect in the Ru(T) centre representing a Ru^+ ion in octahedral coordination of hydride ions.

The EPR spectrum of the Ru(A) centres had an axially symmetric angular dependence appropriate to tetragonal distortion of the Ru^+ ion's local symmetry which is probably a consequence of some intrinsic defects in the LiH(D) host.

This result shows that ruthenium ions can be incorporated in the LiH(D) lattice as substitutional ions. Their oxidation state may change reversibly under the influence of visible light.

Further studies on ruthenium impurity centres in lithium hydride and deuteride require an investigation of their optical properties. This investigation is under way at present.

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