Mo^{5+}-H and W^{5+}-H centres in $ZnWO_4$ single crystals characterized by ESR and ENDOR spectroscopy

Mo^{5+}–H and W^{5+}–H centres in ZnWO$_4$ single crystals characterized by ESR and ENDOR spectroscopy*

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Abstract. ESR and ENDOR methods are used to characterize a new Mo^{5+}–H centre with C$_1$ symmetry in reduced ZnWO$_4$:Mo single crystals. Present ENDOR results also confirm that for the recently reported W^{5+}–H centre in UV- or γ-irradiated ZnWO$_4$:Li crystal an observed superhyperfine interaction results from a nearby hydrogen nucleus. Comparison of spin-Hamiltonian parameters shows the similarity of Mo^{5+}–H and W^{5+}–H centres in ZnWO$_4$ crystals.

1. Introduction

Zinc tungstate (ZnWO$_4$) is known as a scintillator [1–3] and laser host [4] material. Besides its practical application it is of interest to study the nature of point defects prior to and after different treatments and irradiations. In addition to monovalent (Li and Na), divalent (Fe, Mn, Cu, Co and Rh) and trivalent (Fe, Cr and Pt) impurity ions substituting for Zn^{2+}, where some of them cause optical absorption in the range of the intrinsic luminescence decreasing light output, Mo^{6+} was shown to be a detrimental impurity because of its disturbing luminescence and long decay time [5]. The presence of Mo as an impurity ion has also been proved by electron spin resonance (ESR) studies; x-irradiation of undoped ZnWO$_4$ crystals at 77 K initiated electron transfer to Mo^{6+} creating Mo^{5+} ions. These paramagnetic colour centres were assigned to Mo^{5+} ions in C$_2$ symmetry substituting probably for W^{6+} ions and preserving the normal lattice environment of the host ions [6]. Irradiation with 1.5 MeV electrons at 300 K produced, besides the intrinsic V$_O^{\cdot}$ centre (electron trapped at an oxygen vacancy) [7], an Mo-perturbed version of the V$_O^{\cdot}$(B) centre designated as the V$_O^{\cdot}$(B)Mo$_W$ centre [8]. Recently in Li-doped ZnWO$_4$, having a high substitutional OH$^-$ impurity concentration, a W^{5+}-type centre was found after illumination by UV light or γ-radiation at 77 K. An ESR study of this centre indicated only C$_1$ symmetry. Based on one of the observed superhyperfine (SHF) interactions it was stated that probably a nearby hydrogen caused the symmetry reduction; the centre was denoted as W^{5+}–H [9].

The import of this work is to continue clarifying the structure of point defects in Li- or Mo-doped ZnWO$_4$ (enhancing the effect of Li and Mo impurities); particularly to verify with ENDOR (electron nuclear double resonance) the presence of H in the structure of the

* Dedicated to Professor Georg Voelkel on the occasion of his 60th birthday.

W^{5+}–H centre, and to report ESR and ENDOR findings on a similar centre (Mo^{5+}–H) in reduced $ZnWO_4$:Mo crystals.

2. Experimental methods and crystal structure

Single crystals of $ZnWO_4$ were grown in air by a balance-controlled Czochralski technique using Pt crucibles [10]. The raw materials were analytical grade ZnO (REANAL) and WO_3 chemically produced from analytical grade Na_2WO_4 [11]. The crystals were doped by adding 10^{-3} mol mol^{-1} MoO_3 or Li_2CO_3 powder to the melt. Thermal reduction was performed in an argon atmosphere in the presence of carbon cotton at about $960\,°C$ for 5 hours. X-irradiation was done with 150 kV and 20 mA for 1 h at 77 K. ESR and ENDOR measurements were carried out using a Bruker spectrometer model ESP 300 E. For fitting the experimental data the computer program 'VisualEPR' by V Grachev was used.

Zinc tungstate is a monoclinic crystal and it has the space group C_{2h}^4 ($P2/c$) with two formula units per unit cell [12]. The two zinc and the two tungsten ions in a unit cell are magnetically equivalent having C_2 local symmetry. Impurity centres at the Zn or W sites without any nearby lattice defects will conserve the original C_2 symmetry of the lattice site giving only one ESR spectrum for an arbitrary orientation of the magnetic field B. If the centre is accompanied by a nearby imperfection in the lattice, the local symmetry will be reduced to C_1. Then the number of spectra is increased to two according to the two geometrically different defect sites (except for B orientations in the (010) plane or along crystallographic axes for which orientations the two spectra are superposed).

3. Results and discussion

3.1. ENDOR of W^{5+}–H centres

In the present investigation it turned out that the W^{5+}–H centre (with C_1 symmetry) which was produced by UV illumination or γ-irradiation at 77 K [9] could also be created by x-irradiation for 1 hour at this temperature. Its ESR spectrum consisted of main lines due to centres with no W HF or SHF interactions and satellite lines due to one strong ^{183}W HF and one weak ^{183}W SHF interaction. Also all of the main and satellite lines are doubled; this effect was attributed to a perturbing hydrogen near the W^{5+} ion giving an H SHF interaction. To confirm this interpretation ENDOR spectra on one of the main ESR lines were obtained in this work. For SHF splittings smaller than the nuclear Zeeman interaction (such as in the present example), in first order the two ENDOR lines corresponding to $m_s = +\frac{1}{2}$ states are centred around the Larmor frequency of the interacting nucleus. This mean frequency is equal to 24.42 MHz for B along [100]. The measurement was made at 571.6 mT and at this magnetic field the value of the hydrogen Larmor frequency is 24.34 MHz. The agreement of the two frequencies proves directly that the disturbing nucleus near the W^{5+} is a hydrogen, indeed, as it was assumed in [9].

For determination of the spin-Hamiltonian parameters of the hydrogen SHF interaction, angular variations of the ENDOR spectra were taken in four different planes. The spin Hamiltonian employed was

$$\mathcal{H}_s = \mu_B S \cdot \tilde{g} \cdot B + S \cdot \tilde{A}_H \cdot I_H - g_N \mu_N B \cdot I_H \tag{1}$$

where $S = \frac{1}{2}$, $I_H = \frac{1}{2}$ and $\tilde{A}_H$ represents the H SHF interaction tensor. The computer-fitted spin-Hamiltonian parameters of the W^{5+}–H centre with C_1 symmetry are shown in table 1. The angular variations of the ENDOR spectra of the H ions in three different
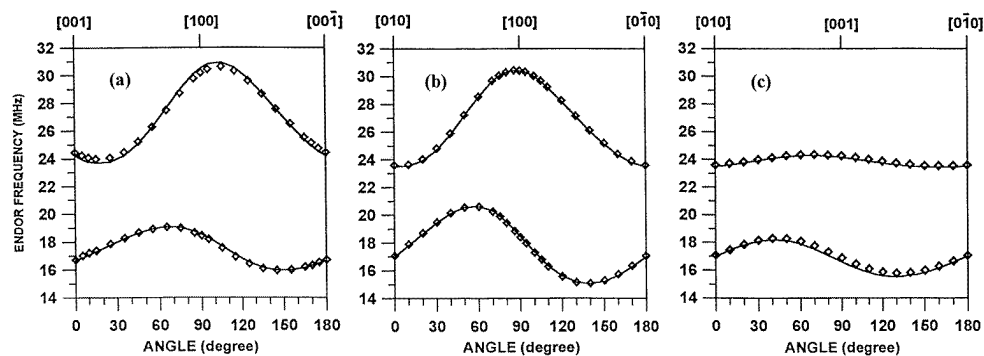
Figure 1. ENDOR angular variations of the W^{5+}–H centre in the ZnWO$_4$:Li crystal (the variations of only one geometrical site are presented). Observations were made at 12 K. Squares represent experimental data and the solid curves are computer-simulated angular variations calculated with the optimized spin-Hamiltonian parameters. The figures correspond to B along (a) [001], [100] and [00$\bar{1}$] directions for 0, 90 and 180°, respectively; (b) [010], [100] and [0$\bar{1}$0] directions for 0, 90 and 180°, respectively; (c) [010], [001] and [0$\bar{1}$0] directions for 0, 90 and 180°, respectively.

planes are shown in figure 1 (for only one geometrical site in each plane and the two ENDOR curves correspond to $m_s = \pm\frac{1}{2}$ states) where squares represent experimental data and the solid curves are computer-simulated angular variations calculated with the optimized spin-Hamiltonian parameters.
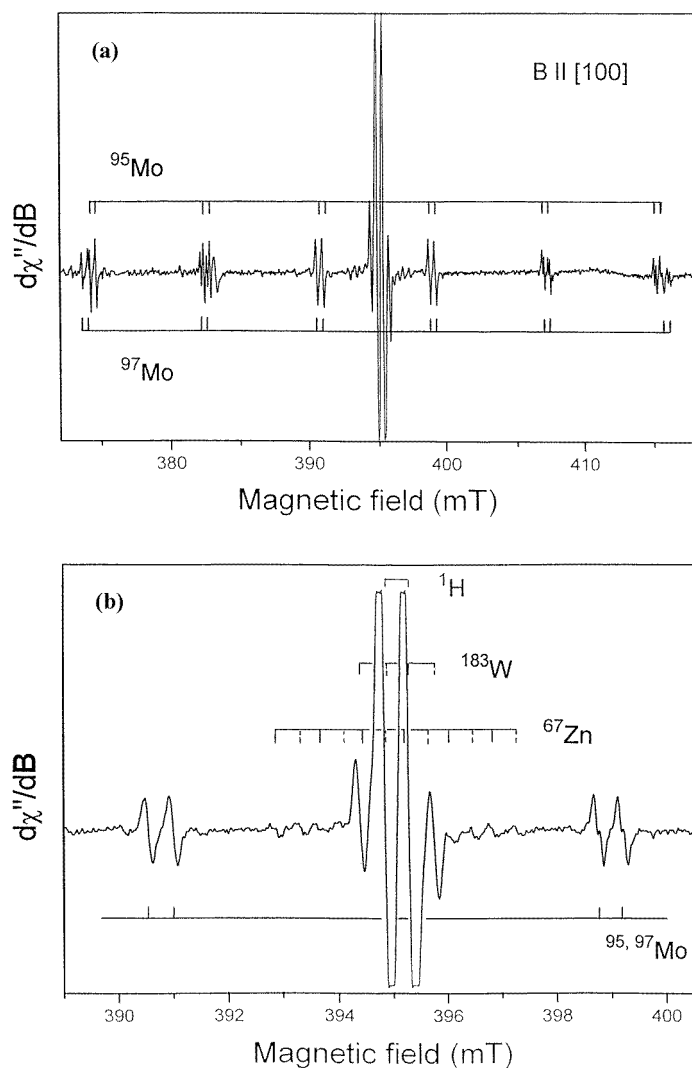
3.2. ESR and ENDOR of Mo^{5+}–H centres

A centre having C$_1$ symmetry and closely resembling the above W^{5+}–H centres was found in the reduced ZnWO$_4$:Mo crystal (in addition to the Mo^{5+} centre in C$_2$ symmetry published earlier [6]). Because of this similarity the new defect is denoted as the Mo^{5+}–H centre. This defect could not be produced by UV illumination at 77 K; however it was also present in reduced *undoped* ZnWO$_4$. As mentioned in the introduction Mo was shown to be an impurity in undoped ZnWO$_4$ [5, 6]; therefore the appearance of Mo-related centres is not surprising in undoped crystals.

The characteristic HF structure due to the electron interaction with the central Mo nucleus enabled identification of the new centre as an Mo centre. Figure 2(a) shows the ESR spectrum for $B \parallel [100]$ where the two spectra due to the C$_1$ symmetry coincide. Around the main line group there are six smaller line groups typical for HF interactions with nuclear spin $I = \frac{5}{2}$. In fact the isotopes ^{95}Mo (abundance 15.72%) and ^{97}Mo (abundance 9.46%) each have $I = \frac{5}{2}$. The magnetic moments of the two isotopes are not equivalent; therefore one expects two sets of six lines. Most of the Mo ions correspond to isotopes with $I = 0$ (abundance 74.82%); hence they produce no sextet splittings but just contribute to the main lines.

However, since as shown in figure 2(a) there is a doubling of the number of lines discussed above, one can assume an SHF interaction due to an isotope with $I = \frac{1}{2}$ (nearly 100% abundant). Since the splitting is small, the nucleus might be expected to be a hydrogen ($I = \frac{1}{2}$, abundance 99.98%) which is in the form of an OH$^-$ ion in the neighbourhood of the central Mo ion. ENDOR study of this interaction proves that, similarly to the model proposed for the W^{5+}–H centre, the responsible nucleus is H. The mean frequency of the

Table 1. Best-fit spin-Hamiltonian parameters of the W^{5+}–H and Mo^{5+}–H centres are presented for comparison with the principal g values and eigenvectors of the $V'_O(B)$ and $V'_O(B)Mo_W$ centres in $ZnWO_4$ single crystals. The A(HF) principal values are given in the Mo centre for ^{95}Mo only. The A(HF) values are given in units of 10^{-4} cm^{-1}; the A(SHF) values obtained from ENDOR are in MHz. The g and A_W(HF) values for the W^{5+}–H centre were taken from [9], while the A_H(SHF) results are from the present work. The direction cosines of the dimensionless eigenvectors are defined with respect to the crystallographic axes [100], [010] and [001], respectively. The estimated uncertainties for eigenvector components of the $\tilde{g}$, $\tilde{A}_{Mo}$, $\tilde{A}_W$ and $\tilde{A}_H$ tensors for the Mo^{5+}–H centre are ±0.001, ±0.001, ±0.003 and ±0.01, respectively, and that of the $\tilde{A}_H$ tensor for the W^{5+}–H centre is ±0.01.

Centre	$\tilde{g}$			$\tilde{A}$(HF) $\times 10^{-4}$ cm^{-1}			$\tilde{A}_W$(SHF) $\times 10^{-4}$ cm^{-1}			$\tilde{A}_H$(SHF) (MHz)			Refs.
	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{yy}	A_{zz}	
Mo^{5+}–H	1.9021± 0.0001	1.8250± 0.0001	1.7021± 0.0001	28.2± 0.1	32.0± 0.1	79.8± 0.1	22.2± 0.1	26.0± 0.1	30.0± 0.1	1.8± 0.3	2.9± 0.3	14.8± 0.3	this work
	0.096	−0.178	0.979	0.575	−0.226	0.786	0.516	0.850	0.116	−0.43	−0.32	0.85	
	0.778	−0.601	−0.185	0.757	−0.217	−0.616	0.750	−0.386	−0.536	0.89	−0.30	0.34	
	0.621	0.779	0.081	0.310	0.950	0.046	−0.413	0.359	−0.837	0.14	0.90	0.41	
W^{5+}–H	1.4911± 0.0005	1.3718± 0.0005	1.1513± 0.0005	58.5± 2.0	61.3± 2.0	148.7± 2.0				5.2± 0.3	6.1± 0.3	14.4± 0.3	[9] and this work
	0.163	−0.282	0.946	0.52	−0.18	0.84				−0.46	−0.28	0.85	
	0.767	−0.567	−0.301	0.81	−0.20	−0.54				0.86	−0.39	0.33	
	0.621	0.774	0.124	0.26	0.96	0.04				0.24	0.88	0.42	
$V'_O(B)Mo_W$	1.8195	1.8448	1.9318										[8]
	0.252	−0.163	0.954										
	0.967	0.011	−0.254										
	0.031	0.987	0.160										
$V'_O(B)$	1.5409	1.5710	1.8185										[7]
	0.236	−0.105	0.966										
	0.825	−0.504	−0.257										
	0.513	0.858	−0.032										

Figure 2. ESR spectrum of the Mo^{5+}–H centre for B along [100] in the reduced ZnWO$_4$:Mo crystal ($T = 35$ K and $\nu \sim 9.44$ GHz). (a) ^{95}Mo and ^{97}Mo HF lines are indicated in the stick diagram. The lines are further split into doublets by H SHF. (b) The central part of the previous spectrum where only the two innermost Mo HF lines (due to ^{95}Mo and ^{97}Mo) are shown. These lines and the H, ^{183}W and ^{67}Zn SHF splittings are indicated by stick diagrams.

ENDOR lines in the spectrum for $B \parallel$ [100] is 16.91 MHz, while the H Larmor frequency for the experimental magnetic field of 395.5 mT is 16.84 MHz. This close agreement again proves the interacting nucleus as to be H.

Figure 2(b) shows the central part of the spectrum presented in figure 2(a). Here one recognizes an SHF interaction with a ^{183}W isotope ($I = \frac{1}{2}$, 14.3% abundant) resulting in the doublet around each of the main lines; this is indicated by a stick diagram. The intensity ratio of one of these lines to a main line is 1:12 as expected for ^{183}W (based on isotopic abundancies). Due to the H SHF only one line of each W SHF doublet is resolved.

Between the main lines and the innermost Mo HF lines on both sides beside the W SHF, four lines of much weaker intensity are visible. These are attributed to SHF interaction with a neighbouring ion of ^{67}Zn ($I = \frac{5}{2}$, abundance 4.12%). This interpretation is illustrated by the stick diagram in figure 2(b), where two six-line patterns are shown, which are separated due to H SHF. The intensities of these Zn lines were too small to obtain their angular variations.

For determination of the spin-Hamiltonian parameters of the Mo^{5+}–H centre the angular variations of the ESR and ENDOR spectra were obtained. The spin Hamiltonian employed was

$$\mathcal{H}_s = \mu_B \boldsymbol{S} \cdot \tilde{\boldsymbol{g}} \cdot \boldsymbol{B} + \sum (\boldsymbol{S} \cdot \tilde{\boldsymbol{A}}_i \cdot \boldsymbol{I}_i - g_N \mu_N \boldsymbol{B} \cdot \boldsymbol{I}_i) \tag{2}$$

where i denotes in turn each interacting nucleus (Mo, H and W). The Mo HF and W SHF interactions can be treated separately since they come from interactions with *one* nucleus of non-zero nuclear spin. Because of the small natural abundancies of the Mo and W isotopes with non-zero nuclear spins, the lines due to interactions with *two* nuclei of such Mo and W isotopes should be 12 times smaller in intensity, and they were not observed. The doubling of all lines due to the H SHF interaction can be overcome in the analysis by averaging the corresponding two lines. In (2), $S = \frac{1}{2}$; $I_{Mo(95)} = \frac{5}{2}$; $I_W = I_H = \frac{1}{2}$; $\tilde{\boldsymbol{A}}_{Mo}$ denotes the HF tensor for ^{95}Mo (HF interaction with ^{97}Mo has been neglected); and $\tilde{\boldsymbol{A}}_W$ and $\tilde{\boldsymbol{A}}_H$ are SHF tensors for W and H nuclei, respectively. The spin-Hamiltonian parameters were determined by fitting the angular variations in four different planes. The average values of the two central lines and the ^{95}Mo HF lines (also averaged for the H doubling) are shown for one plane in figures 3(a) and 3(b), respectively. The angular variations of the H SHF splittings determined by ENDOR are shown for three planes in figure 4. The best-fit parameters of the Mo^{5+}–H centre are given in table 1, in comparison with those of the W^{5+}–H centre.
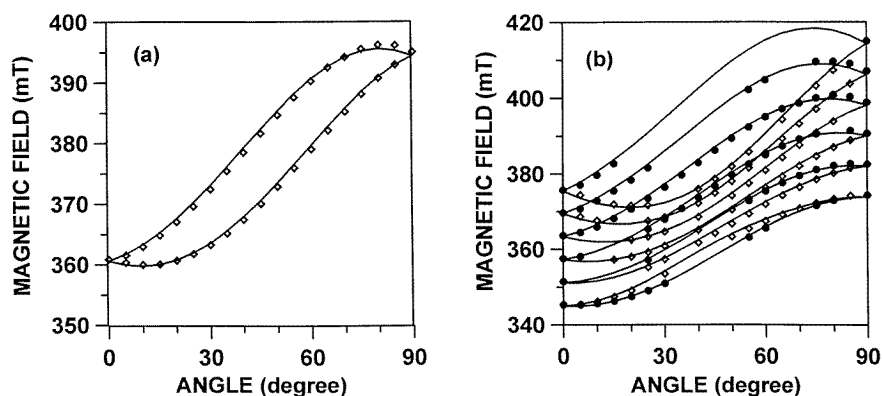
Figure 3. ESR angular variations of the Mo^{5+}–H centre in the $ZnWO_4$:Mo crystal (the lines of both geometrical sites are presented). Symbols represent experimental data and the solid curves are computer-simulated angular variations calculated with the optimized spin-Hamiltonian parameters. The figures correspond to $\boldsymbol{B}$ along [010] and [100] for 0 and 90°, respectively. Observations were made at 35 K and 9.44 GHz. (a) Angular variation of the average of the main ESR lines with no HF or SHF splitting. (b) Angular variation of the ^{95}Mo HF lines (the experimental data of the two geometrical sites are distinguished by squares and circles).
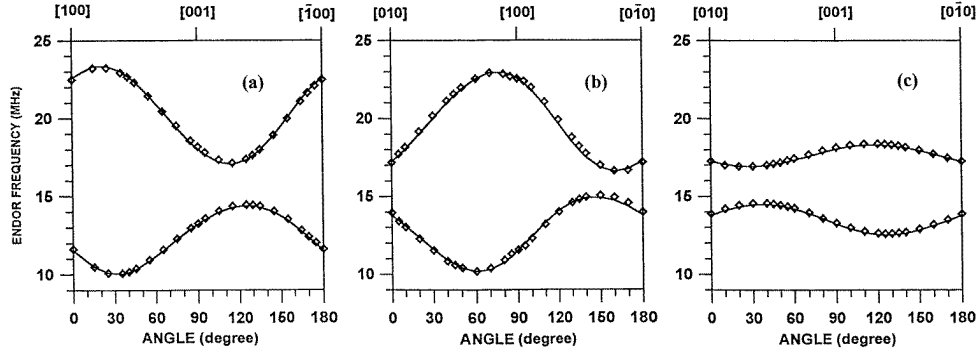
Figure 4. Angular variations of the H ENDOR lines of the Mo^{5+}–H centre (the lines of only one geometrical site are shown). Squares represent experimental data and the solid curves are computer-simulated angular variations calculated from the optimized spin-Hamiltonian parameters. Observations were made at 24 K. The figures correspond to B along (a) [100], [001] and [$\bar{1}$00] directions for 0, 90 and 180°, respectively; (b) [010], [100] and [0$\bar{1}$0] directions for 0, 90 and 180°, respectively; (c) [010], [001] and [0$\bar{1}$0] directions for 0, 90 and 180°, respectively.

3.3. Comparison of W^{5+}–H and Mo^{5+}–H centres

From a comparison of the spin-Hamiltonian parameters (table 1) it is easy to see the similarity of all available corresponding eigenvectors of the different tensors confirming the same basic structure for the W^{5+}–H and Mo^{5+}–H centres. Since the principal g values are smaller than that of the free electron ($g_e = 2.0023$) the Mo centre must be also an electron-excess centre. The principal g values for the Mo^{5+}–H centre deviate less from g_e than those for the W^{5+}–H centre. This results from the larger spin–orbit coupling constant of tungsten compared to that of the molybdenum (λ_W and λ_{Mo} are 2700 and 900 cm^{-1}, respectively [13]); the ratio of the two ($g_{avg} - g_e$) values for these defects is approximately three, which is also the ratio of the respective λ values.

Values of HF and SHF interactions with W, Mo and H, as obtained for the two centres, are most suitably presented in a transformed form: $\tilde{A} = a\tilde{I} + \tilde{B}$, where a, $\tilde{I}$ and $\tilde{B}$ are the isotropic hyperfine coupling constant (proportional to the spin density on the specific nucleus), the unit tensor and the traceless tensor of the anisotropic hyperfine coupling, respectively. We use the diagonalized components: $B_{xx} = -b + b'$, $B_{yy} = -b - b'$ and $B_{zz} = 2b$ where b is the axial part and b' is the measure of the deviation from axial symmetry. The following HF parameters were obtained in units of 10^{-4} cm^{-1}:

W HF(W^{5+}–H)	$a = 89.5$	$b = 29.6$	$b' = -1.4$
Mo HF(Mo^{5+}–H)	$a = 46.7$	$b = 16.6$	$b' = -1.9.$

The values in units of MHz for the H SHF interactions were:

H SHF(W^{5+}–H)	$a = 8.6$	$b = 2.9$	$b' = -0.45$
H SHF(Mo^{5+}–H)	$a = 6.5$	$b = 4.2$	$b' = -0.51.$

The above parameters have the same order of magnitude and relative signs for the two centres indicating similar structures.

The H SHF interactions are small for both centres compared to those of metal hydrides but they are comparable with those of metal–OH$^-$ bonds [14]. The introduction of hydrogen into the crystals as OH$^-$ ions is a reasonable assumption since the crystals were grown in

air; infrared spectroscopy has confirmed the presence of different forms of OH^- centres in $ZnWO_4$ [15, 16]. However, since oxygen is a major element of the host crystal, it is not indicated in the defect designation.

The model for the centres studied is the following: a W^{6+} (or Mo^{6+}) captures an electron and because of the presence of a nearby OH^- ion the centre is locally neutral; it is designated as W^{5+}–H (or Mo^{5+}–H). Nearby W and Zn host ions also contribute to the SHF structure of these centres. There are similarities between these new H-related centres and that of previously reported $V_O^{\cdot}(B)$ centres. Note that for the $V_O^{\cdot}(B)$ centre there is an anion vacancy between two nearest W ions (or between an Mo substituting for W and the nearest W) which has captured an electron. It is believed that the anion vacancy in the $V_O^{\cdot}(B)$ (or $V_O^{\cdot}(B)Mo_W$) centre is probably in the same position as the OH^- ion in the W^{5+}–H (or Mo^{5+}–H) centre. This is supported by the similar eigenvectors shown in table 1 for both H-related centres and $V_O^{\cdot}(B)$ centres. The published eigenvectors for the latter centres have been transformed according to the crystal symmetry to facilitate comparisons. The deviation of the zz principal axis directions is 9.2° for the $V_O^{\cdot}(B)$ and W^{5+}–H centres; the deviation for the $V_O^{\cdot}(B)Mo_W$ and Mo^{5+}–H centres is 6.3°. This comparison tends to support the models for the W^{5+}–H and Mo^{5+}–H centres. Also the similarity in structure for these H-related centres gives evidence for Mo being substitutional for W.

The different methods needed for creating the two hydrogen-related centres can be explained with the proposed defect model. The W^{5+}–H centre is produced in Li-doped $ZnWO_4$ where plain substitutional OH^- anions are present [9]. These OH^- ions have W neighbours since these are host ions in the crystal. When UV or X irradiation liberates electrons, they will be captured at those W ions which have OH^- neighbours, thus producing the W^{5+}–H centre which is locally neutral (charge compensated). When Mo^{6+} substitutes for W^{6+}, no charge compensation is needed; thus there is only a small probability for OH^- ions to be near to Mo dopant ions. This is why the Mo version of the centre cannot be produced by UV or x-irradiation at 77 K. These radiations are not energetic enough to produce ionic displacements. Therefore high temperature is required for the diffusion of a hydrogen toward the Mo ion which has trapped an electron in the reducing atmosphere.

4. Summary

In the Mo-doped $ZnWO_4$ crystal after a reducing treatment at about 960 °C a new $S = \frac{1}{2}$ paramagnetic centre in C_1 symmetry was created; it has been characterized by ESR and ENDOR spectroscopy. The typical double-sextet structure due to the two different Mo isotopes having non-zero nuclear spins allowed assignment of the centre to an Mo^{5+} ion. Its spin-Hamiltonian parameters showed close similarity to those of the recently published W^{5+}–H centre and therefore the centre was designated as an Mo^{5+}–H centre. ENDOR studies proved that in both of these centres the perturbing defect nearby was a hydrogen in an OH bond.

Acknowledgments

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