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Electron spin resonance of vanadium- and molybdenum-perturbed V_{O} centres in ZnWO_4 single crystals

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Abstract. Two new dopant-related defects which are similar to one another have been found by ESR in vanadium-doped and molybdenum-doped zinc tungstate single crystals. These defects resemble the $V_{\text{O}}(\text{B})$ centre (an electron associated with an oxygen vacancy) reported earlier for electron-irradiated undoped ZnWO_4 . However, the new centres are significantly modified by a perturbing vanadium or molybdenum dopant ion which substitutes for a tungsten cation neighbouring the trapped electron.

1. Introduction

Technological interest in zinc tungstate (ZnWO_4) has been enhanced by its use as a scintillator crystal for detecting x-rays, γ -rays and particle rays [1–3]. Because these rays can generate changes in the defect structure of the crystal and modify its luminescence efficiency, investigations of radiation-induced centres are important for the evaluation and development of the scintillator material. Furthermore, impurities are known to influence the scintillation process as well as the nature of the colour centres produced by irradiations. In this paper we report electron spin resonance (ESR) investigations on two new impurity-related defects, one in vanadium-doped and the other in molybdenum-doped ZnWO_4 crystals, where these two defects have similar characteristics. However, the V-related[†] defect is detected in the *as-grown* crystal whereas the Mo-related defect is detected only after electron irradiation.

1.1. Radiation-induced defects

Recent reports on the effects of radiation on nominally pure ZnWO_4 have been made [4, 5]. It was found that irradiation with high-energy electrons at 300 K produced two electron-excess defects which were labelled $V_{\text{O}}(\text{A})$ and $V_{\text{O}}(\text{B})$ centres (using the notation of Kröger *et al* [6]), where for each a single electron is trapped at an oxygen vacancy [4]. However, the spin is not localized at the vacancy; instead it exhibits a diffuse wavefunction similar to the F^+ centres in alkaline-earth oxides [7]. These two electron-excess centres in ZnWO_4

[†] A different font (\mathcal{V}) is employed for vanadium throughout this paper to distinguish it from usage here and in prior journal articles where V represents a vacancy and \mathcal{V} represents a hole-like centre.

differ in their oxygen vacancy positions and thus were denoted (A) and (B). The only hole-like defect detected in electron-irradiated ZnWO_4 was identified as a hole trapped at an O^{2-} ion near a zinc vacancy [4]. In a different study on an undoped ZnWO_4 crystal, x-ray irradiation at 15 K transferred electrons to Mo^{6+} impurity ions, forming Mo^{5+} electron-excess centres in C_2 symmetry and also two types of paramagnetic hole centres [5]. One of the hole centres was attributed to an intrinsic defect corresponding to a hole trapped at an oxygen ion. The other was identified as a V_{OH} centre, which consists of a hole trapped at an O^{2-} ion with a neighbouring zinc vacancy and an OH^- ion in an adjacent O^{2-} site. However, for the work presented here, electron-excess Mo-related centres in C_1 symmetry are found in electron-irradiated ZnWO_4 (for both Mo-doped and undoped crystals) where the defects resemble $V_{\text{O}}(\text{B})$ centres.

1.2. Defects via doping

ESR studies have been published for each of the following divalent or trivalent (dopant or impurity) metal ions in ZnWO_4 : Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} (all referenced in [8]), and also Ti^{3+} [9], Pt^{3+} [10], Rh^{2+} [10, 11] and Gd^{3+} [12]. The papers state that these ions substitute for divalent Zn and preserve the C_2 symmetry of the Zn site. A V^{4+} ion is the only dopant ion of charge state higher than 3^+ reported to substitute for a zinc ion [13] and it was proposed that the observed lower symmetry (C_1) was caused by a nearby charge-compensating Zn vacancy. In contrast, for the work presented here on V-doped ZnWO_4 it is found that the vanadium occupies a tungsten site.

2. Crystal structure

Zinc tungstate belongs to a class of divalent monoclinic tungstates with small cations; this class also includes MgWO_4 , MnWO_4 , CoWO_4 and NiWO_4 . It has the space group C_{2h}^4 ($P2/c$) with two formula units per unit cell [14, 15]. The two zinc and two tungsten sites in a unit cell are magnetically equivalent and the ions of each element have C_2 local symmetry. Defect centres at sites of either of the host cations without any nearby lattice defects will conserve the original C_2 symmetry and show only one ESR spectrum for an arbitrary orientation of the crystal. However, the number of spectra is increased to two (except for orientations in the (010) plane or along directions parallel to the crystallographic axes) if the defect is accompanied by a local charge compensator such as a Zn or O vacancy; then the local symmetry is reduced to C_1 .

3. Experimental details

Single crystals of ZnWO_4 were grown in air by a balanced-controlled Czochralski technique using platinum crucibles [16, 17]. The crystals were doped by adding either V_2O_5 or MoO_3 powder in the ratio 10^{-3} mol mol $^{-1}$ to the melt. Electron irradiations were accomplished using a Van de Graaff accelerator operated at 1.5 MV with nominal sample current densities of 3–6 $\mu\text{A cm}^{-2}$ for times up to 1 h. Irradiations were made at room temperature (RT); however, the sample temperature was not controlled and some sample heating presumably occurred. ESR measurements were performed at 90 K for the vanadium and 35 K for the molybdenum centres, using a Varian X-band spectrometer.

4. Experimental results

4.1. $ZnWO_4$ doped with vanadium

For an arbitrary orientation of the *as-received* $ZnWO_4:V$ crystal, the ESR spectrum consisted of six eight-line hyperfine (HF)[†] patterns which collapsed to three sets of eight lines for the magnetic field direction in the (010) plane or for the field parallel to any of the crystallographic axes. The spectra indicated three separate defects, each having spin $S = 1/2$, residing in two inequivalent sites (C_1 symmetry), and exhibiting a HF interaction with an approximately 100% abundant $I = 7/2$ isotopic species. These are spectra that might be expected for $3d^1 V^{4+}$ ions, where the HF patterns are characteristic of the ^{51}V isotope ($I = 7/2$; 99.8% abundance). In this paper we present results only on that vanadium centre with the largest concentration, which permitted detailed measurements of HF angular variations. An ESR recording at 90 K for $B \parallel [001]$ is shown in figure 1; the eight-line ^{51}V HF of the most concentrated vanadium defect is labelled. Each HF line exhibits smaller doublet lines of equal intensities centred about it. The doublets are labelled in figure 1 but only for the three lowest-field V HF lines. This structure results from an additional HF interaction with a nuclear spin $1/2$, which is attributed to the 14.3% abundant ^{183}W isotope with $I = 1/2$. The intensity ratio of a V HF line to a doublet line, averaged from expanded field sweeps, is about 13:1, which agrees well with the 12:1 ratio expected for ^{183}W .

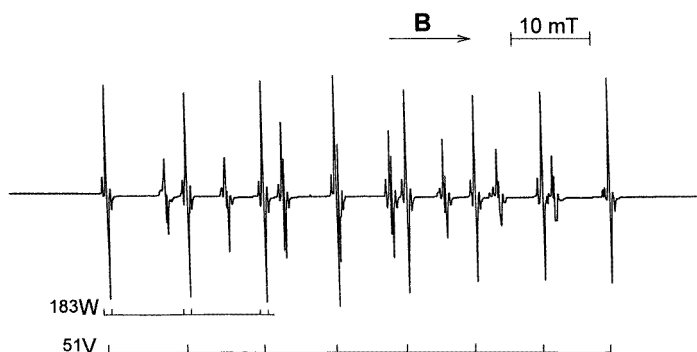


Figure 1. ESR spectrum of vanadium-related centres in V-doped $ZnWO_4$ for $T \simeq 90$ K, $\nu \simeq 9.1$ GHz and $B \parallel [001]$. The ^{51}V eight-lined HF pattern and three of the best resolved ^{183}W HF splittings are indicated with tick marks for the most concentrated V-related centre. The extra lines are due to additional V centres not discussed herein.

Angular variations of this V-related centre were obtained for three different planes as shown in figure 2(a), 2(b) and 2(c), where they correspond to rotation of the crystal about the [010], [001] and [110] directions, respectively. The orientation denoted by the vector f in figure 2(c) is about 39° away from the [100] direction measured in the (001) plane. The spin Hamiltonian for the centre can be expressed as

$$\mathcal{H}_s = \mu_B S \cdot \tilde{g} \cdot B + S \cdot \tilde{A} \cdot I + S' \cdot \tilde{A}' \cdot I' + I \cdot \tilde{P} \cdot I - g_N \mu_N B \cdot I \quad (1)$$

where $S = 1/2$, $I = 7/2$ for the \tilde{A} HF interaction and $I' = 1/2$ for the \tilde{A}' HF interaction. Spin-Hamiltonian parameters were determined using a least-squares fitting of the angular variations in the line positions and they are presented in table 1. The nuclear

[†] In this paper the practice will be to denote all electron–nuclear interactions simply as HF. No distinction will be made between HF and superhyperfine (SHF) until defect models have been discussed.

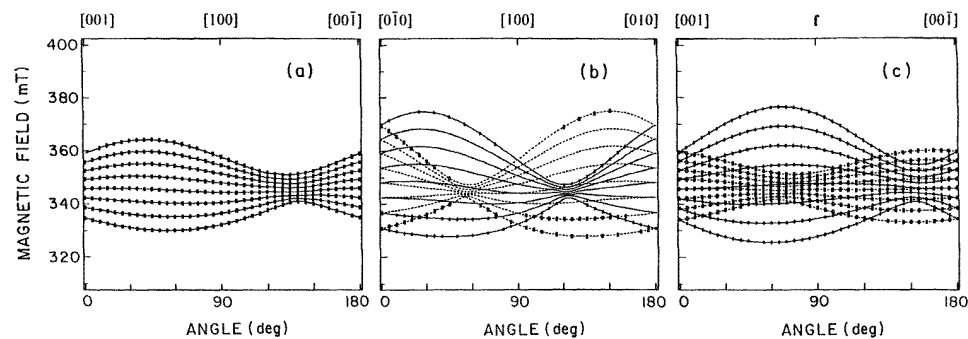


Figure 2. Angular variations in the ^{51}V HF lines for the most concentrated V-related centre in a $\text{ZnWO}_4:\text{V}$ crystal. Observations were made at 90 K and about 9.1 GHz. The angles 0° , 90° and 180° correspond to \mathbf{B} along the directions indicated at the top of the figures. The variations are for (a) the (010) plane, (b) the (001) plane and (c) the (110) plane, where the vector \mathbf{f} is about 39° away from the [100] direction measured in the (001) plane. The point symbols represent experimental data and the solid curves are computer-simulated angular variations calculated with the optimized spin-Hamiltonian parameters.

quadrupole components for $\tilde{\mathbf{P}}$ were the same order of magnitude as the uncertainties in their determination; therefore they are not included in the table. In figure 2 the point symbols represent experimental data and the solid curves are calculated angular variations using optimized spin-Hamiltonian parameters.

4.2. ZnWO_4 doped with molybdenum

Prior to any kind of irradiation the Mo-doped ZnWO_4 crystals did not show any Mo-related ESR spectra. After electron irradiation, besides the signals due to earlier published centres [4], a new type of spectrum was detected. It is shown in figure 3 for $\mathbf{B} \parallel [001]$ and 35 K. In arbitrary orientations the whole spectrum is doubled, indicating two different geometries for the centres and thus C_1 symmetry. Each spectrum consists of a main line and a pair of satellite lines symmetrically arranged about the main line. The doublet lines each show an average intensity ratio relative to the main line of approximately 1 to 12, again indicating an interaction with a ^{183}W nucleus. Also a set of six equally spaced small lines centred about the main line is shown, indicating a HF interaction with a nucleus of $I = 5/2$ (figure 3). In fact Mo has two isotopes having $I = 5/2$: ^{95}Mo (15.9% abundant) and ^{97}Mo (9.6% abundant). The ratio of their nuclear magnetic moments is $\mu(^{97}\text{Mo})/\mu(^{95}\text{Mo}) = 1.02$. Because of the small difference in the Mo magnetic moments and the relatively small A -values, corresponding HF transitions due to the two isotopes are not resolved. The intensity ratio of the HF lines to the main line is expected to be about 1 to 18, which agrees with averaged measurements. Some additional lines appear in figure 3 which result from undetermined defects.

To determine the spin-Hamiltonian parameters for the Mo centre the spin Hamiltonian given by equation (1) was used, where $S = 1/2$, $I_{\text{Mo}} = 5/2$ and $I'_W = 1/2$. The quadrupole effect was neglected since the quadrupole moments of the Mo isotopes are quite small. Angular variations of the Mo-related centre were measured in three different planes to permit determination of the spin-Hamiltonian parameters given in table 1. These variations are shown just for the (001) plane, where figure 4(a) represents the variations in the main lines

Table 1. For $ZnWO_4$ single crystals the table provides a comparison of spin-Hamiltonian parameters of the $V_O(B)$ centre [4], the $V_O(B)$ centres perturbed by vanadium or molybdenum (present work), and the $Mo^{5+}(C_2)$ centre [5]. The direction cosines of the dimensionless eigenvectors reading downwards are defined with respect to the crystallographic axes [100], [010] and [001], respectively. The estimated uncertainties for the present work are as follows: ± 0.0002 for g -values; ± 0.003 for eigenvectors of $\tilde{\mathbf{g}}$; $\pm 2 \times 10^{-4} \text{ cm}^{-1}$ for A - and A' -values; ± 0.003 and ± 0.01 for eigenvectors of $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{A}}'$, respectively.

Centre	g_{xx}	g_{yy}	g_{zz}	A_{xx} (10^{-4} cm^{-1})	A_{yy} (10^{-4} cm^{-1})	A_{zz} (10^{-4} cm^{-1})	A'_{xx} (10^{-4} cm^{-1})	A'_{yy} (10^{-4} cm^{-1})	A'_{zz} (10^{-4} cm^{-1})
$V_O(B)$	1.5409	1.5711	1.8185	36.9	68.2	96.4	21.6	23.0	28.0
	0.236	-0.105	0.966	-0.333	0.367	-0.869	0.68	-0.74	0.04
	-0.825	0.504	0.257	0.612	-0.617	-0.495	0.71	0.63	-0.32
	-0.513	-0.858	0.032	0.717	0.697	0.019	0.21	0.25	0.95
$V_O(B)V_W$	1.8912	1.9372	1.9728	9.5	37.1	130.3	12.6	14.1	16.0
	0.368	0.161	0.916	-0.862	0.067	-0.502	0.80	-0.59	-0.12
	-0.917	0.226	0.329	-0.474	-0.459	0.752	0.54	0.78	-0.33
	-0.154	-0.961	0.230	-0.180	0.886	0.428	0.28	0.20	0.94
$V_O(B)Mo_W$	1.8195	1.8448	1.9318	0.	25.	35.	23.4	24.0	30.0
	0.252	0.163	0.954	-0.705	0.689	-0.167	0.90	-0.43	0.11
	-0.967	0.011	0.254	0.431	0.230	-0.872	0.44	0.81	-0.40
	0.031	-0.987	0.160	0.563	0.687	0.459	0.09	0.41	0.90
$Mo^{5+}(C_2)$	1.7666	1.7497	1.6277	20.4	46.3	70.1			
	0.995	0.000	0.105	0.996	0.000	0.259			
	0.000	-1.000	0.000	0.000	-1.000	0.000			
	0.105	0.000	-0.995	0.259	0.000	-0.966			

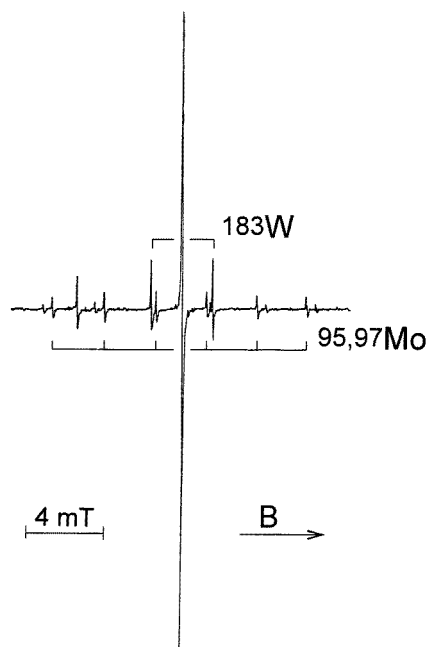


Figure 3. ESR spectrum of the Mo-related center in electron-irradiated Mo-doped ZnWO₄ for $T \simeq 35$ K, $\nu \sim 9.1$ GHz and $B \parallel [001]$. The ^{95,97}Mo HF and the ¹⁸³W HF splittings are indicated; however, the HF patterns for ⁹⁵Mo and ⁹⁷Mo are superposed. The extra lines are due to other defects.

and the W HF, and figure 4(b) shows the variations in the Mo HF lines. The solid curves represent calculated values based on the computer-fitted spin-Hamiltonian parameters; these compare favourably with the experimental points.

The spectrum of the Mo centres also appeared with low intensity in an *undoped* electron-irradiated sample which was kept at RT for several weeks. As reported earlier, Mo has been found by ESR to be a low concentration impurity in our ZnWO₄ crystals [5].

5. Discussion

The appearance of paramagnetic vanadium centres of spin 1/2 in V-doped ZnWO₄ suggests that a substantial portion of the V is present in the crystal as V⁴⁺. However, the centres observed are distinctly different from the single V⁴⁺ defect previously reported by Krygin *et al* [13], where they conclude that the V substitutes for Zn. In this study we contend that the V substitutes for W rather than Zn based upon the fairly strong ¹⁸³W HF interaction observed. For divalent and trivalent paramagnetic cations substituting for Zn, usually no W HF can be resolved (Cu is the sole exception and its W HF parameter was given as $A = 0.37$ mT [18]). Moreover, for a V ion in a W site the nearest cations are two W ions which could provide W HF interaction. The difference between the current results and those in [13] may derive from different methods employed in doping the crystals. For the ZnWO₄ crystals investigated here, V₂O₅ was added to the melt, whereas Krygin *et al* used VOWO₄ to dope their crystals; for both studies the crystals were grown by the Czochralski method. We have found no evidence of the defect reported in [13].

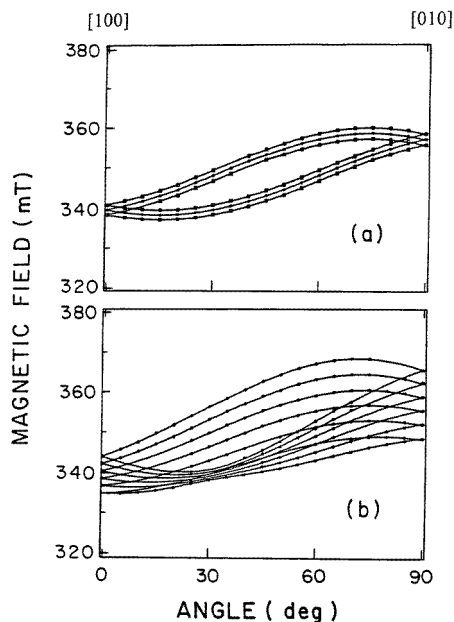


Figure 4. Angular variations for the Mo centre in an electron-irradiated $ZnWO_4:Mo$ crystal. Observations were made at 35 K and about 9.1 GHz. The angular variations are for (a) the main lines and W HF lines and (b) the Mo HF lines. The symbols represent experimental data and the solid curves are computer-simulated angular variations calculated with the optimized spin-Hamiltonian parameters.

Since the ESR spectra of the V centre indicate that it has C_1 symmetry, a symmetry-lowering perturbation must be nearby. It is reasonable to assume that this is a charge-compensating oxygen vacancy (V_O) between the V ion that substitutes for W and one of the two nearest W ions; therefore these two W ions neighbouring the V become inequivalent. The large V HF interaction and smaller but substantial W HF interaction indicate that the spin density is not localized on the V but is diffuse. The character of this centre closely resembles that of the $V_O(B)$ centre reported for electron-irradiated undoped $ZnWO_4$ [4]. Spin-Hamiltonian parameters of both types of centres are given in table 1; by a comparison of the eigenvectors of their \tilde{g} tensors and tungsten \tilde{A} tensors the similarity of the centres is evident. Therefore it is deduced that this V centre can be described as a V-perturbed $V_O(B)$ centre and it will be denoted as $V_O(B)V_W$. To assist the interpretation of this V-related centre, the model previously offered for the $V_O(B)$ centre [4] is presented in figure 5(a). In this model the electron is trapped at an oxygen vacancy (designated by B) and its diffuse wavefunction interacts unequally with the two neighbouring tungsten ions shown as W_1 and W_2 . For the $V_O(B)V_W$ centres, whose proposed model is given in figure 5(b), a V ion has substituted for the tungsten ion W_1 that yields the stronger HF interaction for the $V_O(B)$ centre. During the crystal growth, oxygen vacancies adjacent to V impurity ions enter the lattice to charge compensate for V^{4+} ions in W^{6+} ion sites. However, because of the presence of the oxygen vacancy the spin density is shifted significantly from the V ion towards this vacancy and the neighbouring W.

The Mo is believed to enter the lattice as Mo^{6+} where it substitutes for W^{6+} . After electron irradiation it becomes paramagnetic and exhibits Mo HF and W HF interactions.

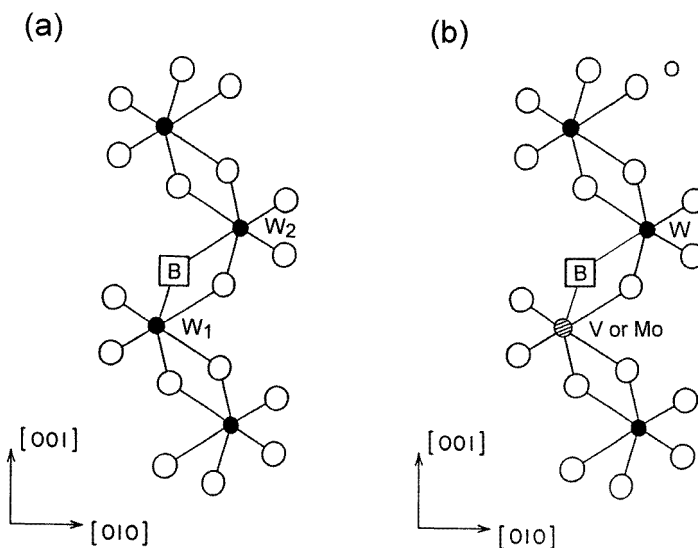


Figure 5. (a) Model for the $V_O(B)$ centre in electron-irradiated undoped $ZnWO_4$ which corresponds to an electron trapped in the oxygen-ion vacancy B [4]. (b) Model for the $V_O(B)V_W$ centre in V-doped $ZnWO_4$ where a V ion has substituted for the tungsten W_1 shown in (a). The $V_O(B)Mo_W$ centre in electron-irradiated Mo-doped $ZnWO_4$ is represented by this same model with the Mo substitution shown.

Also, because of its C_1 symmetry, again one needs to invoke a nearby perturbing defect, which is assumed to be an oxygen vacancy contributing to partial charge compensation. The W HF interaction for this Mo centre contrasts with the absence of an observable W HF for the Mo^{5+} centre which exhibits C_2 symmetry in $ZnWO_4$ [5]. For the latter centre there is no nearby defect and the spin is strongly localized on Mo, as is evident from its larger Mo HF parameters (provided for comparison in table 1) and its lack of a W HF interaction. However, for the new Mo centre with C_1 symmetry the Mo HF parameters are smaller, and fairly large W HF parameters are obtained. This finding indicates that the spin density is less concentrated on the Mo nucleus and is shifted towards the oxygen vacancy and the neighbouring W. This defect is similar to the $V_O(B)V_W$ defect discussed above although its concentration of spin density on the W is greater. Comparisons of eigenvectors of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}'$ (W HF) tensors for the $V_O(B)$ centre, the $V_O(B)V_W$ centre and the new Mo centre show that they are all similar. Thus we conclude that the new Mo centre is also a perturbed $V_O(B)$ centre and label it as $V_O(B)Mo_W$. Its proposed model is also represented by figure 5(b). During growth the Mo enters the lattice as a diamagnetic Mo^{6+} ion substitutional for W^{6+} . Then oxygen vacancies are generated during electron irradiation. An oxygen vacancy with one trapped electron adjacent to the Mo ion is required for the $V_O(B)Mo_W$ defect. For presentation throughout this paper we have denoted all electron–nuclear interactions as HF rather than SHF. However, SHF designations, as used previously for the $V_O(B)$ centre [4], are judged more appropriate than HF for the new defects. Their models are based upon substantial delocalization of the electron trapped at the oxygen vacancy, yielding prominent electron–nuclear interactions with ligand cations.

6. Summary

Two dopant-perturbed defects with ESR characteristics similar to the radiation-induced electron-like $V_O(B)$ centre [4] have been discovered in unirradiated V-doped and electron-irradiated Mo-doped $ZnWO_4$ single crystals. Spin-Hamiltonian parameters have been determined. Each defect can be described as an unpaired electron trapped at an O vacancy like the $V_O(B)$ centre but where each is modified by the dopant ion. The diffuse nature of the electron's wavefunction is indicated by SHF interactions with an adjacent dopant ion and with an adjacent W ion. Models have been proposed and the defects have been labelled as $V_O(B)V_W$ and $V_O(B)Mo_W$ centres.

Acknowledgments

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