

Growth Defect  $W^{3+}\cdot W^{2+}$  of  $CdWO_4$  Crystals

M. V. Chernov, V. A. Nadezhny, and A. A. Pavlyuk

Institute of Inorganic Chemistry, Russian Academy of Sciences, Novosibirsk, Russian Federation

Received October 8, 2006; revised August 15, 2007

**Abstract.**  $CdWO_4$  crystals grown by the Czochralski method at the low-temperature gradient were investigated with electron spin resonance (ESR) spectroscopy. ESR spectra did not contain the signals of impurity ions typical for the  $CdWO_4$  structure, i.e.,  $Fe^{2+}$ ,  $Mn^{2+}$ , and  $Ti^{3+}$ . At the same time, in the studied crystals a complex ESR spectrum having the hyperfine structure due to four equivalent nitrogen nuclei was observed ( $W^{14}$ ;  $I = 1/2$ ; natural abundance, 14.22%). Angular dependence analysis and simulation of ESR spectra bear witness that this signal originates in defects by a spin-Hamiltonian with the following parameters:  $D = 0.16$  G,  $A = 0.6$  G,  $g_{\parallel} = 2.01$ ,  $g_{\perp} = 1.97$ ,  $g_{\parallel} = 1.927$  and electron spin  $S = 1/2$ . There is one magnetically nonequivalent position of the center of the crystal structure and the direction of  $D_{\parallel}$  and  $g_{\parallel}$  coincides to the direction of  $W_{\parallel}W_{\perp}$  for  $Cd_4(Cd_{1-x}W_x)_4O_{12}$  in the crystal structure. Because of the fact that it is physically impossible to observe the electron spin  $S = 1/2$  for the defect if one established signal has not lying into nearest site then the such electron spin is realized for one magnetically inequivalent nitrogen atom, we suggest the defect structure to be the pairs  $W^{3+}\cdot W^{2+}\cdot W^{2+}$ . In the structure of this defect the ion  $W^{3+}$  is surrounded, the ions  $W^{2+}$  and  $W^{2+}$  have electron spin  $S = 1/2$  and  $S = 1/2$ , respectively. The necessary condition for such defect to exist is to place the center of ions in defect position for the charge compensation. The reason for such defect to form is supposed to be the incorporation of  $W^{3+}$  into lattice of  $CdWO_4$  buffer. The presence of  $W^{3+}$  and  $W^{2+}$  in Cd position in the defect structure provides the charge compensation and the lowering of the lattice stress.

## 1 Introduction

The recent interest in the chalcogen tungstate crystals is defined by their scintillating properties which surpass the properties of the BGO crystal, the most frequently used scintillating crystal in high-energy radiation detectors. As tungstates with trivalent cations (Mg, Ca, Ni, Pt, Zn, Mn, Gd) tungstate tungstate crystal-lites with the wolframite structure. The X-ray analysis of the structure into electron data  $CdWO_4$  crystals have monoclinic symmetry with lattice parameters  $a = 0.502$  nm,  $b = 0.585$  nm,  $c = 0.507$  nm,  $\beta = 91.5^\circ$  [1]. The  $Cr^{3+}$  [2],  $Fe^{3+}$  [3] and  $Mn^{2+}$  [4] ions were investigated by electron spin resonance (ESR) in the structure of this crystal. As it is assumed now, these ions substitute chalcogen in the regular lattice of  $CdWO_4$ . Trivalent ions of elements  $Cr^{3+}$  appear after annealing at a temperature of 700°C in the oxygen-containing atmosphere. The annealing at this

temperature does not evoke the diffusion of the uranium or tungsten and their removal from the bulk crystal but does evoke the diffusion of the oxygen into the crystal that provides the charge compensation and changes the valency of chromium ion up to the  $\text{Cr}^{3+}$  state [2]. It is known that the uranium oxide vapor pressure is higher than that of tungsten oxide at the temperature of crystal synthesis. Therefore, the starting concentration of the uranium oxide in the furnace charge is usually loaded abundantly.

One of the necessary characteristics of the crystals which are used as the scintillators is the absence of the defects which produce the energy levels in the forbidden gap affecting the scintillating characteristics (the wave length and the lifetime of excited state). This work presents the results of the ESR investigation of a novel defect in the  $\text{CaWO}_4$  structure, which arises during the crystal growth.

### 3 Experimental

The crystals of  $\text{CaWO}_4$  were grown by the Czochralski method with a low-temperature gradient [5]. This method of crystal growth was developed by the Institute of Inorganic Chemistry, Russian Academy of Sciences, Novosibirsk. The crystals investigated were synthesized from the alloy containing the oxides of tungsten and uranium. The abundance of  $\text{CaO}$  amounts to 1%, that was intentionally introduced to compensate the difference between the oxide vapor pressures of tungsten and uranium and in this way to achieve stoichiometry. The growth of the crystals was provided over the seed crystal along the crystal  $c$ -axis. The crystals are uncolored and transparent without any visible inclusions and defects.

The ESR spectra were obtained on an automatic spectrometer E-109 Varian in the X- and Q-band at 77 and 300 K.

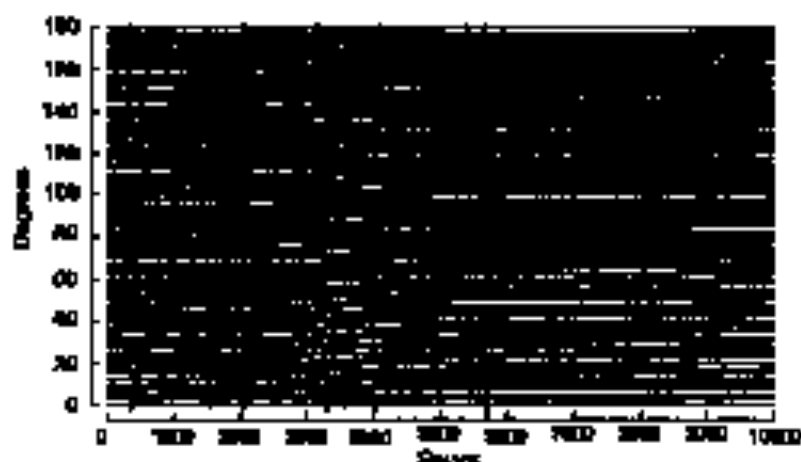


Fig. 1. Angular dependence of the ESR spectrum in  $\text{CaWO}_4$  obtained in the  $bc$ -plane. The spectra were taken at  $T = 77$  K in the 9.2 GHz band.

In the crystals investigated, the ESR spectra of paramagnetic ions of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Cr^{3+}$  were absent. A novel complex ESR spectrum was found. The corresponding angular dependence in which this spectrum was observed is shown in Fig. 1. At 77 K the ESR lines become narrow and around the main lines for symmetrical systems of weak satellites becomes observable. In Fig. 2 one of the ESR lines is given with its satellites. The spectrum was taken in the arbitrary orientation of the specimen with respect to the magnetic field direction in the X-plane. The analysis of the intensity profile between the central line and its satellites has shown that these weak satellites are caused by the hyperfine structure of two nonequivalent tungsten ions (the isotope of tungsten with the nuclear spin  $I = 1/2$ ; natural abundance, 14.2%). In this case two magnetically nonequivalent positions of the hyperfine structure of the center are observed at 77 K. The ratio between the hyperfine-structure parameters of the two nonequivalent tungsten ions does not depend on the orientation and equals 4:3.

The spectrum taken at 9.5 GHz has an extremely complex angular dependence with angular-dependent intensity (Fig. 1). Therefore the angular dependence of the spectrum was investigated at 35.5 GHz and that obtained in the  $h_0$ -plane is given in Fig. 3a. The maximal splitting in the spectrum is observed when the direction of the magnetic field is located in the  $h_0$ -plane along the  $Cd_1-Cd_{10}$  (or  $W_1-W_{10}$ ) direction. Several transitions are observable in the ESR spectrum with two magnetically nonequivalent positions of the center. This number of transitions corresponds to the electron spin  $S = 7/2$ . We based experimentally found parameters into the developed program (6) that allows us to calculate the ESR spectrum and to simulate the ESR spectra and their angular dependence regarding of the ratio between the terms in the spin Hamiltonian corresponding to different interactions. By varying them we have optimized the fine-structure parameters and simulated the angular dependence of the novel ESR spectrum. The simulated angular dependence of the ESR spectrum is shown in Fig. 3b.

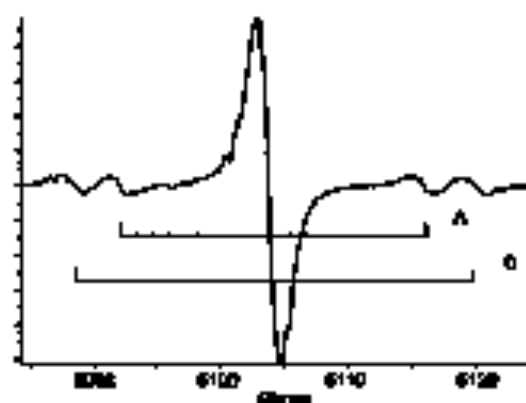


Fig. 2. Hyperfine structure of the ESR spectrum of  $CdWO_4$  caused by the interaction with the isotopes  $W^{2+}$  having the nuclear spin  $I = 1/2$ . The spectra were measured in an arbitrary orientation at  $T = 77$  K at the 9.5 GHz band. A, hyperfine structure of the  $W^{2+}$  ion; B, hyperfine structure of the  $W^{3+}$  ion.

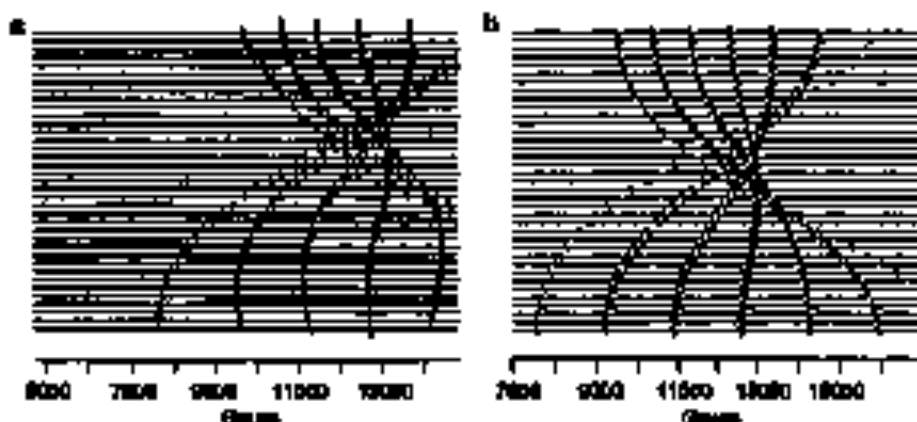


Fig. 2. Experimental (a) and simulated (b) angular dependence of the ESR spectrum of  $\text{CdWO}_4$ . Excitation spin is  $S = 7/2$ . The experimental angular dependence is obtained in the  $z$ -plane. The spectra were taken at  $T = 300$  K in the 31.5 GHz band.

The spectrum is described by the spin Hamiltonian

$$\mathcal{H}^S = g_B \beta H S_z + D(S_z^2 - 1/3 S(S+1)) + E(S_x^2 - S_y^2), \quad (1)$$

with parameters  $S = 7/2$ ,  $g_B = 2.01$ ,  $g_p = 1.97$ ,  $g_n = 1.987$ ,  $D = 935$  G, and  $E = 90$  G.

The presence of two nonequivalent tungsten sites in the defect structure with spin  $S = 7/2$  leads to two paramagnetic centers of tungsten ions with different electron spins. The possible variants of these states are  $S_1 = 2$ ,  $S_2 = 3/2$  ( $W^{2+}$ ,  $W^{3+}$ ) and  $S_1 = 5/2$ ,  $S_2 = 1$  ( $W^{3+}$ ,  $W^{4+}$ ), which give the total spin  $S = 7/2$ .

### 3 Discussion of Results

The actual type of the paramagnetic defect of cadmium tungstate crystals with  $S = 7/2$  is very complex for its ESR spectrum interpretation. The analysis of possible variants of this electron state shows that  $S = 7/2$  could be realized by an  $f$  ion, e.g.,  $\text{Ce}^{3+}$  [7]. However, no  $f$  ion has the crystal field  $F = 1/2$  and two isotopes with the natural abundance of 16.2%. It is a priori obvious that this electron spin cannot be realized by only one transition ion. The observed hyperfine structure of two nonequivalent tungsten ions indicates the presence of two signals that in the defect structure and corresponds to different charge states of tungsten ions and their different electron spins. The complexity of this case is defined by the fact that besides the dipole-dipole interaction between paramagnetic fragments of the defect, each of them resides in the crystal field of the nearest oxygen neighborhood, therefore it is impossible to separate the contributions of these effects with the  $g$ -factor and the parameters of the crystal field of each ion are

known. In the general case the ESR spectrum of the coupled pair is described by the spin Hamiltonian constructed from the spin Hamiltonians of the individual ions:

$$c\mathcal{H}^2 = \beta H g S + S D S + I_1 A_1' S + I_2 A_2' S, \quad (2)$$

with  $S = a g_1 + b g_2$ ,  $D = c D_1 + \beta D_2 + a d$  and  $A_1' = a d_1$ ,  $A_2' = b d_2$ , where  $a = S_1/(S_1 + S_2)$ ,  $b = S_2/(S_1 + S_2)$ ,  $c = S_1(2S_1 - 1)/(S_1 2S_1 - 1)$ ,  $\beta = S_2(2S_2 - 1)/(S_2 2S_2 - 1)$ ,  $d = 2S_1 S_2 / (S_1 2S_1 - 1)$ ,  $D_1$ ,  $D_2$ ,  $d_1$ ,  $d_2$ ,  $A_1$  and  $A_2$  are parameters of individual ions.

Coupled pairs of transition metal ions are very interesting objects but not an often met case. For example, Kulagya (8) described  $Mn^{2+}\cdot Cu^{2+}$  and  $Ni^{2+}\cdot Co^{2+}$  coupled pairs, whose partners in pairs differed in their cases and had different electron states. Both cases are described well by the spin Hamiltonian Eq. (2).

In the investigated case, the ratio  $A_1'/A_2' = 4/3$  (see Fig. 2) and  $S = 7/2$  correspond to the electron spins  $S_1 = 2$  and  $S_2 = 3/2$  of individual ions. It seems that two tungsten ions have charge states  $W^{2+}$  and  $W^{3+}$ . The observed  $L$  and  $S$  parameters and  $g$ -values are effective parameters. It is impossible to separate pairs of  $g$ -values and parameters of the crystalline field of  $W^{2+}$  and  $W^{3+}$  ions because in the literature no information about  $W^{2+}$  and  $W^{3+}$  ionic electron states of tungsten is obtain.

The minimum of the defect contains two tungsten ions. According to the principal direction of the hyperfine-structure tensor and the number of magnetically nonequivalent positions, the tungsten ions must occupy the positions over one oxygen octahedron, not in neighboring ones, as it is shown in Fig. 4.

The tungsten ions in the regular  $CdWO_4$  lattice have the charge state  $W^{6+}$  and are diamagnetic. It is very difficult to form the charge state of  $(W^{2+}\cdot W^{3+})$  configuration in tungsten regular positions, because in this case at least three oxygen ions must be removed from the lattice intermediate octahedron to ensure electric neutrality. An odd electron state supports an additional charge compensation of oxygen ions, e.g., by the formation of the OH-group. The IR spectra investigation has revealed the absence of OH-groups, i.e., this charge configuration is hardly realized in the regular tungsten position. If one takes into account that the vapor pressure of cadmium oxide is higher than the pressure of tungsten oxide, then one can assume that the missing deficit of the cadmium ions is compensated by the tungsten ions. Therefore the most probable defect model is that where the charge states  $W^{2+}\cdot W^{3+}$  are realized in the regular position of cadmium. The presence of the  $W^{3+}$  can be explained with the charge compensation by a univalent cation in the intermediate octahedron (between the tungsten ions). Among these univalent cations is the potassium ion, which can penetrate the crystal from the melt that the tungsten was extracted from. According to this concept, the defect must be formed when the univalent cation incorporates into the regular position of cadmium, and for the charge compensation the trivalent cation is required to be incorporated in the neighboring cation position. The existence of only one magnetically nonequivalent position of the paramagnetic defect in the crystal lattice (as seen from Fig. 3) means that the  $W^{2+}\cdot W^{3+}$  pairs can be directed only along the direction of the lattice cation chain. Cadmium

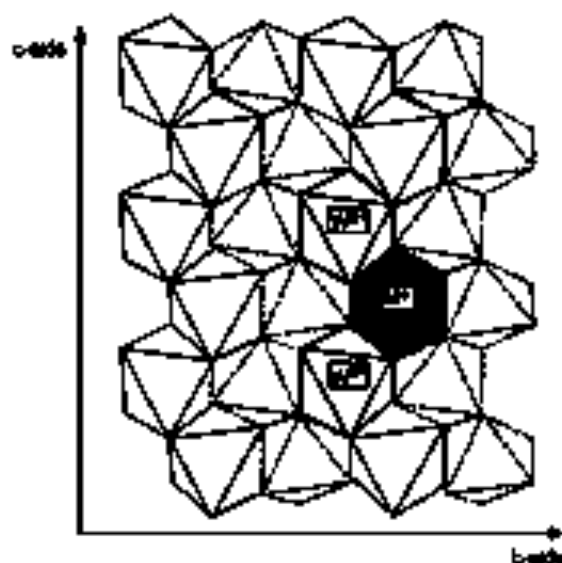


Fig. 4. Structure of the defect in the  $\text{CaWO}_4$  crystal. Dashed outlines are the oxygen octahedra around the tungsten ions in the regular positions, solid-line outlines are those of the defective ions.

ions close to the univalent ion are supposed to be replaced by bi- and trivalent tungsten ions. This variant of the defect model provides charge compensation and lowering of the lattice stress.

In spite of the fact that the  $\text{W}^{5+}\text{-W}^{6+}$  ions may be directed only in such a way and one magnetically nonequivalent position of the fluor structure is evident, two magnetically nonequivalent positions of the hyperfine structure are observed because the directions of principal values of the hyperfine tensor and the fine-structure tensor are different (the first position we  $\text{W}^{5+}$  when the  $\text{W}^{5+}$  and  $\text{W}^{6+}$  ions are placed as shown in Fig. 4, the second position we  $\text{W}^{6+}$  when tungsten ions swap their places). In Fig. 4 these magnetically nonequivalent positions of the hyperfine structure of each group of ESR lines (caused by the hyperfine interaction with the nuclei of  $\text{W}^{5+}$  and  $\text{W}^{6+}$  ions) are to be observed.

#### 4. Conclusions

A novel ESR spectrum of a paramagnetic defect with the spin  $S = 7/2$  was found during the investigation of uniaxial  $\text{CaWO}_4$  crystals. We have established the structure of this center (Fig. 4) and the parameters of the corresponding spin Hamiltonian. The ESR investigation of this center has shown that it is formed by the coupled pair  $\text{W}^{5+}\text{-W}^{6+}$ , located in regular octahedral sites positions. In this case, the formation of this pair assumes the presence of an univalent tungsten ion between the tungsten ions. Such univalent center can be potassium ions, present in the initial components of the furnace charge.

**References**

1. Chichagov A.P., Ilyukhin V.V., Belov N.V.: Dokl. Akad. Nauk USSR **166**, 87–89 (1966)
2. Andreeva E.V., Karlov N.V., Manenkov A.A., Milyaev V.A., Shirkov A.V.: Solid State Phys. (Leningrad) **6**, 1649–1653 (1964)
3. Kedzie R.W., Kestigan M.: Appl. Phys. Lett. **3**, 86 (1963)
4. Donovan R.E., Vuylsteke A.A.: Phys. Rev. **127**, 76–77 (1962)
5. Pavlyuk A.A., Stenin Yu.G. in: Book of Abstracts of the 5th International Conference on Inorganic Scintillators SCINT99 (Mikhailin V., ed.), p. 147. Moscow: Moscow State University 1999.
6. Cherney N.V., Nadolinny V.A., Boguslavsky E.G.: Zavod. Lab. **69**, 169–175 (2003)
7. Hempstead C.F., Bowers K.D.: Phys. Rev. **118**, 131–134 (1960)
8. Buluggiu E.: J. Phys. Chem. Solids **41**, 43–45 (1980); *ibid.* **41**, 1175–1180 (1980)

**Authors' address:** Nikolay V. Cherney, Institute of Inorganic Chemistry, Lavrent'eva avenue 3, Novosibirsk 630090, Russian Federation