SOVIET PHYSICS JETP VOLUME 22, NUMBER 3 MARCH, 1966

ELECTRON PARAMAGNETIC RESONANCE OF THE TETRAHEDRAL COMPLEX $[MnF_4]^{2-}$ *IN SCHEELITE*

L. V. BERSHOV, A. S. MARFUNIN, and R. M. MINEEVA

Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences, USSR

Submitted to JETP editor April 9, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 49, 743-746 (September, 1965)

A new EPR spectrum in natural scheelite is investigated; the spectrum is associated with the tetrahedral complex $[MnF_4]^{2-}$, which replaces $[WO_4]^{2-}$ in scheelite ($CaWO_4$). The spectrum can be described by a spin Hamiltonian of tetragonal symmetry; the values of the spin Hamiltonian constants are determined.

In recent years the optical and microwave spectra of scheelite ($CaWO_4$) containing trace amounts of rare-earth and iron-group ions have been intensively investigated in connection with the application of scheelite as a working laser material. The EPR spectra of the following ions in scheelite have been described: Mn^{2+} and Gd^{3+},[1] Eu^{2+},[2] Tb^{3+},[3] Yb^{3+},[4] and Nd^{3+}.[5,6]

The impurity ions are usually isomorphically substituted for the divalent cation Ca^{2+} in the scheelite structure. The local symmetry then either remains tetragonal (Mn^{2+}, Gd^{3+}, Nd^{3+}, and Yb^{3+} replace Ca^{2+} without local charge compensation), or it is reduced to orthorhombic by the replacement of $2Ca^{2+}$ by $M^{3+} + M^{1+}$ in the case of charge compensation.

In scheelite containing Nd^{3+}, an orthorhombic spectrum of four strongly anisotropic lines, attributed to Nd^{3+} located in the WO_4 tetrahedra, was observed[6] together with the spectrum from Nd^{3+} located in Ca sites. (The distortion of the tetrahedra along the four three-fold axes leads to four inequivalent sites.) However, this interpretation has been disputed.[4] In the absence of distortion along the L_3 axes of the tetrahedra, the axial spectra of the ions in Ca and W sites are geometrically indistinguishable (identical local symmetry S_4 with a common Z axis); the orthorhombic spectra of these two sites must obviously be rotated through a small angle, and their appearance is associated with the charge-compensation mechanism. In such cases these spectra can be distinguished only by the characteristics of their spin Hamiltonian constants. Thus, the character of the spectra of impurity ions in scheelite displays a complex dependence on their introduction into Ca or W sites and on the charge-compensation mechanism (which is regulated by the conditions of synthesis).

We have observed in a single crystal of natural scheelite two different Mn^{2+} spectra, which are naturally attributed to Ca and W sites. One of these spectra has the characteristic "signature" of super-hyperfine structure (shfs) from four F^{19} nuclei. At the same time, the coordination of Mn^{2+} in the second spectrum is definitely tetrahedral. This permits one to obtain the constants of the spin Hamiltonian for Mn^{2+} in W sites, indicating a new charge compensation mechanism in scheelite. Besides this, this is for the present the only compound in which EPR spectra of Mn^{2+} with fluorine ligands in tetrahedral coordination are observed.

The structure of scheelite may be visualized as CaO_8 groups and WO_4 tetrahedra alternating in accordance with the symmetry of the space group C_{4h}^6 ($I4_1/a$). The structure is sketched in Fig. 1, which takes into account the recent neutron-diffraction[7] and x-ray-diffraction[8] refinements of the oxygen positions. Besides the Ca and W sites, one can readily distinguish possible sites for compensating ions or for interstitial paramagnetic ions.

The Ca—O distances are almost identical ($Ca—4O = 2.44$ Å, and $Ca—4O = 2.48$ Å), and $W—4O = 1.788$ Å. The parameters of the oxygen ion are $x = 0.1504$, $y = 0.0085$, $z = 0.2111$; their spacings in the WO_4 tetrahedron are O_1-O_2 $= 2.485$ Å, O_2-$O_3 = 2.880$ Å.[7,8] This indicates a small distortion of the WO_4 tetrahedron along the l_4 axis (the height along this axis should be equal to $(O—O)/2^{1/2} = 2.14$ to 2.11 Å; the experimental height is 1.96 Å).

Both observed Mn^{2+} spectra (they partially

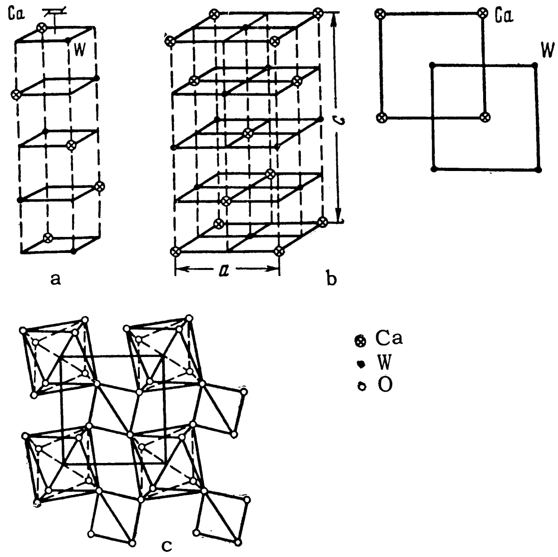

FIG. 1. Scheelite structure: a – alternation of Ca and W sites along the four-fold screw axis b – layer arrangement of Ca and W sites; c – CaO_8 groups and WO_4 tetrahedra.

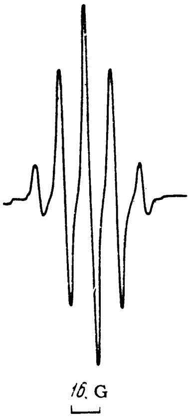

FIG. 2

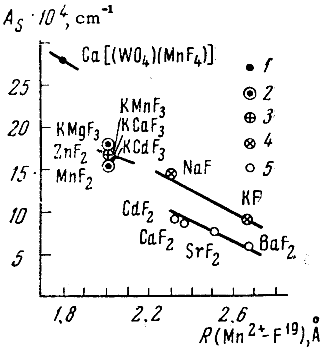

FIG. 3

FIG. 2. Fluorine shfs Mn^{2+}–F^{19}.

FIG. 3. Dependence of the shfs constant A_s^F in fluorides on coordination, structure type, and Mn^{2+}–F^{19} distance. Structure types: 1 – scheelite (coordination number (cn) = 4); 2 – perovskite (cn = 6); 3 – rutile (cn = 6); 4 – NaCl (cn = 6); 5 – fluorite (cn = 8).

overlap) have tetragonal symmetry with a common Z axis, which coincides with the [001] direction in the crystal. The more intense spectrum is identified as that described for Mn^{2+} replacing Ca^{2+},[1] and has the spin-Hamiltonian constants given in Table I (see below).

The second spectrum (its intensity is 1/200 of the first) is characterized by a very large value for the axial component of the crystal field and by the presence of shfs, which consists of five components of relative intensity 1 : 4 : 6 : 4 : 1 (Fig. 2). This is interpreted as being due to the interaction of an unpaired Mn^{2+} electron with four identical nuclei with nuclear spin I = ½ situated at identical distances from the Mn^{2+} ion. In this case, fluorine is practically the only possible ligand ion with nuclear spin ½ . The presence of 0.02% fluorine was confirmed by chemical analysis (colorimetric determination by V. V. Danilova). Thus, these data show that $[WO_4]^{2-}$ is replaced by the complex $[MnF_4]^{2-}$.

Table I. Constants of the spin Hamiltonian of Mn^{2+} in scheelite in Ca sites[1] and W sites (in 10^{-4} cm^{-1})

	b_2^0	b_4^0	b_4^4	$g_\parallel$	$g_\perp$	A	B
Ca	—137,6	—1.2	—11.5	1,99987	1.99980	88,93	89,53
W	(+)380,0	(—)0,2	(—)2,8	1,9955	1.9885	(—)87,5	(—)87,2

Table II. Spin-Hamiltonian constants of Mn^{2+} with fluorine ligands

	Coordination number	Structure Type	M — F, Å	g	A, 10^{-4}cm^{-1}	A_s^F, 10^{-4} cm^{-1}	Reference
BaF_2	8	CaF_2	2.68	2,0015	92.4	5.7	[10]
SrF_2	8	»	2.51	2,0015	95.6	7.9	[10]
CaF_2	8	»	2.36	2.0016	95.8	8.8	[10]
CdF_2	8	»	2.33	2.0026	93.0	9.4	[11]
NaF	6	NaCl	2,31	1.996	91.0	14.4	[12]
KF	6	»	2.67		91,0	9.2	[13]
ZnF_2	6	TiO_2	2.04	2.002		17.0	[14]
MnF_2	6	»	2.12	—	—	15.6	[15]
$KMgF_3$	6	$CaTiO_3$	1,994	2.000	91,2	18.1	[16]
$KCdF_3$	6	»	2.167	2.002	92.6	15.8	[16]
$KCaF_3$	6	»	2.188	2.002	93,1	15.5	[16]
$KMnF_3$	6	»	2,093	—	—	16.3	[17]
$CaMnF_4$	4	$CaWO_4$	1.788	$g_\parallel = 1.9955$ $g_\perp = 1.9885$	87.5 87,2	27.9	—

The spectrum with fluorine shfs is described by a spin Hamiltonian with tetragonal symmetry:

$$\mathcal{H} = b_2^0O_2^0 + b_4^0O_4^0 + b_4^4O_4^4 + g_{\parallel}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + AI_zS_z + B(I_xS_x + I_yS_y), \quad (1)$$

where A is the hyperfine structure (hfs) constant in the parallel orientation, and B the same in the perpendicular orientation. The numerical values of the constants are given in Table I (precision: ±0.0005 for the g factor and $\pm 1 \times 10^{-4}$ cm^{-1} for the other constants).

The components of the shfs tensor are due to the isotropic contact interaction A_S and the anisotropic dipole interaction A_σ:

$$A_s^F = 27.9, \qquad A_\sigma^F = 0.7\cdot 10^{-4}\ \mathrm{cm}^{-1} (\pm 0.5\cdot 10^{-4}\ \mathrm{cm}^{-1}).$$

The obtained constant A (for comparison with the kind of chemical bond, see [9]) in the complex MnF_4 completes the series of tetrahedral structures with different ligands in which this quantity has been measured (in 10^{-4} cm^{-1}, see [9]): $Mn\text{-}Te_4$ (56.0 in ZnTe, 56.4 in CdTe), $Mn\text{-}Se_4$ (60.0 in ZnSe, 61.5 in CdSe), $Mn\text{-}S_4$ (64.0 in ZnS, 63.6 in CdS), $Mn\text{-}O_4$ (77.0 in ZnO), $Mn\text{-}F_4$ (87.5 in scheelite).

The spin-Hamiltonian constants for Mn^{2+} in a number of fluorides are given in Table II. The values obtained in $[MnF_4]^{2-}$ for the g factor and for A (hfs) are the smallest, and that for A_S^F (shfs) is the largest of those observed in these fluorides.

Figure 3 shows the dependence of fluorine shfs on coordination number, structure type and $Mn^{2+}\text{-}F^{19}$ distance.

[1] C. F. Hempstead and K. D. Bowers, Phys. Rev. **118**, 131 (1960).

[2] J. Bronstein and V. Volterra, Phys. Rev. **137**, A1201 (1965).

[3] P. A. Forrester and C. F. Hempstead, Phys. Rev. **126**, 923 (1962).

[4] J. Kirton and R. C. Newman, Phys. Letters 10, 277 (1964).

[5] Kask, Kornienko, Prokhorov, and Fakir, FTT 5, 2303 (1963), Soviet Phys. Solid State 5, 1675 (1963).

[6] R. W. Kedzie and M. Kestigian, Appl. Phys. Letters 4, 124 (1964).

[7] Kay, Frazer, and Almodovar, J. Chem. Phys. **40**, 504 (1964).

[8] A. Zalkin and D. H. Templeton, J. Chem. Phys. **40**, 501 (1964).

[9] L. V. Bershov and A. S. Marfunin, DAN SSSR 155, 632 (1964).

[10] V. M. Vinokurov and V. G. Stepanov, FTT 6, 380 (1964), Soviet Phys. Solid State 6, 303 (1964).

[11] Hall, Hayes, and Williams, Proc. Phys. Soc. (London) 78, 883 (1961).

[12] W. Hayes and D. A. Jones, Proc. Phys. Soc. (London) 71, 503 (1958).

[13] W. J. Veigele and W. H. Tanttila, J. Chem. Phys. 41, 274 (1964).

[14] Clogston, Gordon, Jaccarino, Peter, and Walker, Phys. Rev. **117**, 1222 (1960).

[15] R. G. Shulman and V. Jaccarino, Phys. Rev. 108, 1219 (1957).

[16] S. Ogawa, J. Phys. Soc. Japan **15**, 1475 (1960).

[17] R. G. Shulman and K. Knox, Phys. Rev. Letters 4, 603 (1960).

Translated by L. M. Matarrese

97