

Zero-field splitting of Mn^{2+} ions in scheelites

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The spin-Hamiltonian parameters of the 6S ground state of Mn^{2+} have been measured for seven crystals with scheelite structure in the temperature range 4.2–350 K. The low-temperature values of the zero-field parameters reflecting the contributions from the static lattice are discussed with respect to the usual theories of S -state splitting. The applicability of the superposition model and of different point-charge models is revised. In this particular case the dominant part of the crystal-field contributions can be explained by a relativistic splitting mechanism. The appropriate crystal-field coefficients required are obtained by numerical calculations, the corresponding point charges being related to simple aspects of chemical bonding.

I. INTRODUCTION

Although a considerable amount of experimental data exists on the ground-state splitting of S -state ions in crystals, relatively little progress has been made in obtaining a quantitative understanding of the physical processes which determine the magnitudes of these splittings. Attempts at carrying out complete theoretical analyses have to include many competing contributions of similar magnitude which come from a variety of different mechanisms.^{1,2}

Due to these difficulties a complete and definitive calculation of the ground-state splitting of Mn^{2+} in any crystal has not been reported until now. In order to improve this situation the need for planned and systematic experiments, preferably for a range of isomorphous host crystals, has been emphasized.³

We have carried out such a systematic investigation on the zero-field splitting of Mn^{2+} incorporated in seven different scheelite-type crystals. The temperature dependence of the spin-Hamiltonian parameter b_2^0 can be described using an isotropic-Einstein-oscillator model for the impurity vibration.⁴ At sufficiently low temperature the splitting parameters therefore consist of an appropriate contribution of the zero-point vibration and a truly static part determined by the rigid lattice. These static contributions of the crystal field are the subject of this paper.

II. EXPERIMENTAL

We have taken X -band EPR spectra of Mn^{2+} in the temperature range 4.2 to 350 K. Single crystals have been grown by the Czochralski technique adding relative concentrations of 10^{-3} to 10^{-4} manganese ions to

the melt. The scheelite structure (space group C_{4h}^2) is set up by four formula units AXO_4 in the tetragonal unit cell.

We have investigated tungstates and molybdates ($X = W, Mo$) with divalent cation ($A = Ca, Sr, Pb, Cd$) where Mn^{2+} replaces an equicharged ion. For the barium compounds we did not succeed in this substitution. This was obviously due to the fact that the ionic radii were too varied.^{4,5} $CdWO_4$ crystallizes in the monoclinic structure and so had to be excluded.

The regular cation site in scheelites has the point symmetry S_4 . Since Mn^{2+} does not require charge compensation for incorporation, it is assumed that this symmetry is preserved. Thus a spin Hamiltonian of the form

$$H = g_1(B_x S_x + B_y S_y) + g_{\parallel} B_z S_z + A_1(S_x I_x + S_y I_y) + A_{\parallel} S_z I_z + D(S_z^2 - \frac{35}{12}) + \frac{7}{36} F(S_z^4 - \frac{95}{14} S_z^2 + \frac{81}{16}) + \frac{1}{6} a(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16})$$

is obtained.⁶

Apart from the electronic Zeeman energy and the crystal-field contributions, an axial hyperfine interaction due to the 100% abundant isotope ${}^{55}Mn$ ($I = \frac{5}{2}$) has to be considered and this yields $2S(2I+1) = 30$ allowed EPR transitions. The crystal-field terms can be abbreviated in the shorthand notation of the operator equivalent method to

$$H_{CF} = \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60} b_4^0 O_4^0 + \frac{1}{60} b_4^4 O_4^4,$$

with the relations

$$b_2^0 = D, \quad b_4^0 = \frac{1}{2} a + \frac{1}{3} F, \quad b_4^4 = \frac{5}{2} a.$$

TABLE I. Spin-Hamiltonian parameters at 4.2 K (hyperfine and zero-field parameters in 10^{-4} cm^{-1}). []: Data measured at 80 K.

	A_{\parallel}	A_{\perp}	b_2^0	b_4^0	b_4^4	ϕ_0
CdMoO ₄	-86.84	-88.04	57.7	-0.6
CaMoO ₄	-88.01	-88.93	33.0	-0.5	[-4.9]	[0°]
SrMoO ₄	-89.18	...	24.3	-0.4	[-4.8]	[8.5°]
PbMoO ₄	-87.85	-89.23	72.3	-0.4	[-4.1]	[9.5°]
CaWO ₄	-89.60	89.09	-134.8	-1.5	[-11.5] ^a	[9.0°] ^a
SrWO ₄	-90.47	-90.1 ^b	-108.9	-1.2	-5.3 ^b	19° ^b
PbWO ₄	-88.87	-89.40	-28.9	-1.3

^aReference 6.

^bReference 7.

Using tabulated matrix elements of the irreducible tensor operators O_n^m , energies and positions of resonances are obtained by carrying out perturbation theory to second order. Sets of spin-Hamiltonian parameters measured at 4.2 K are given in Table I together with some values taken from other publications. By lowering the temperature to 1.5 K it was ascertained that the results do not change remarkably below 4.2 K. Some of the parameters could not be determined due to the anisotropy of line shapes.

For the sake of completeness some values for b_4^4 measured at higher temperatures have been included, since this parameter does not show a pronounced temperature dependence. D_0 , the truly static part of the dominant zero-field parameter D , can be obtained by subtracting the (negative) contribution of the zero-point vibration from the corresponding b_2^0 values in Table I. The results are listed in Table II.

Comparing the experimental results, one notices a characteristic difference between tungstates and molybdates which actually ends in a change of sign for the parameter D and, respectively, D_0 . Averaging b_4^4 (as far as possible) and b_4^0 values yields similar differences between the two groups of compounds. Apart from this, g shift and hyperfine splitting are smaller in each molybdate than in the corresponding tungstate. Finally it is worth mentioning that the Mn^{2+} resonances can be saturated more easily in molybdates than in tungstates.

III. DISCUSSION

A. Application of the superposition model

The basic idea of the superposition model (SPM) is to represent a certain spin-Hamiltonian parameter as linear combination of ligand contributions³:

$$b_k^q = \sum_i \bar{b}_k(R_i) K_k^q(\theta_i, \phi_i)$$

K_k^q is a coordination factor determined by the angular position of the corresponding ligand, and $\bar{b}_k(R_i)$ is the "intrinsic" parameter depending upon the distance only. This parameter is supposed to be typical of the kind of chemical bonding between the paramagnetic ion and the ligand. Whereas the K_k^q can be calculated easily if the geometrical data are known, no analytical radial dependence of the intrinsic parameter is prescribed *a priori*. One aim of the model is to find such dependencies empirically by analysis of experimental data. In most cases the application of the SPM has been restricted to 8S states (Gd^{3+} , Eu^{2+}) yielding acceptable consistency of the results.⁸⁻¹² A first application to 6S states has been reported in a recent paper.¹³

Within a group of isomorphous host crystals in which the interionic distances vary only little one may assume a radial dependence of the form

$$\bar{b}_k(r) = \bar{b}_k(R_0) \left(\frac{R_0}{R} \right)^{l_k}$$

TABLE II. Static zero-field parameters of second order (all values in 10^{-4} cm^{-1}).

Sample	CdMoO ₄	CaMoO ₄	SrMoO ₄	PbMoO ₄	CaWO ₄	SrWO ₄	PbWO ₄
D_0	70.8	42.6	34.6	84.4	-128.4	-101.9	-18.0

using an averaged distance R_0 and an optimized exponent t_k . For the cation site in scheelites there are two sets of four oxygen ligands each as nearest neighbors at distances R_1 and R_2 . Therefore the zero-field parameters are written in a modified version¹²

$$b_k^q = \bar{b}_k(R_1) \sum_{i=1}^4 K_k^q(\theta_{1i}, \phi_{1i}) + \bar{b}_k(R_2) \sum_{i=1}^4 K_k^q(\theta_{2i}, \phi_{2i}) .$$

For practical purposes this notation can be shortened to

$$b_k^q = \bar{b}_k(R_0) K_{k\text{eff}}^q ,$$

the "effective" coordination factor $K_{k\text{eff}}^q$ depending upon the exponent t_k chosen.

Some coordination factors have been calculated already by the same authors¹² but erroneous results have been obtained in some cases (wrong sign of K_4^q due to the wrong choice of azimuthal angles). Thus we have repeated these calculations with the available geometrical data being summarized in a preceding paper.⁴ These data have been measured at room temperature whereas structural data taken at helium temperature should be used for an analysis of low-temperature values of spin-Hamiltonian parameters. In this way small systematic errors come into the calculated coordination factors but these seem to be unimportant as there is a certain arbitrariness in the choice of t_k anyway. Apart from this they are supposed to be of little importance for a relative comparison between crystals of the same isomorphous group.

To evaluate the intrinsic second-order parameter \bar{b}_2 from the values given in Table II (using the SPM) one has to choose an appropriate power-law exponent t_2 . For the scheelites doped with Gd^{3+} , $t_2 = 2, 5$ has been proposed.¹² This choice results in values of \bar{b}_2 between $67 \times 10^{-4} \text{ cm}^{-1}$ ($SrMoO_4$) and $167 \times 10^{-4} \text{ cm}^{-1}$ ($PbMoO_4$) for the molybdates, respectively, $-228 \times 10^{-4} \text{ cm}^{-1}$ ($CaWO_4$) and $-69 \times 10^{-4} \text{ cm}^{-1}$ ($PbWO_4$) for the tungstates, showing a rather large variation within each group. Beyond that one observes a characteristic difference of about $200 \times 10^{-4} \text{ cm}^{-1}$ when comparing tungstates to molybdates with the same cation. This leads to opposite signs of \bar{b}_2 and is obviously due to differences in chemical bonding.

The intrinsic parameter \bar{b}_4 for each sample can be determined from the experimental values using either b_4^q or b_4^s . Since the power-law exponent t_4 has to be the same in both cases, the model can be checked for consistency in this way. Where experimental data are available, the results coincide quite well, giving $\bar{b}_4 = (0.3 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$ for molybdates and $\bar{b}_4 = (0.65 \pm 0.10) \times 10^{-4} \text{ cm}^{-1}$ for tungstates. Here the difference between the two groups becomes evident again. As the calculations are not very sensitive

to the choice of t_4 these results are valid for exponents $3 \leq t_4 \leq 5$.

On the whole the superposition model seems to be better suited for the analysis of the $n = 4$ parameters of Mn^{2+} in scheelites than for the $n = 2$ ones which yield less consistent results.

B. Crystal-field approximation

Having evaluated the intrinsic parameters within the framework of the SPM, we must try to relate the results to splitting mechanisms discussed in the literature.

For this purpose we have to calculate the crystal field acting on the Mn^{2+} ion in the scheelites. As experimental data from optical measurements are not available in this case and great difficulties exist in the consideration of polarization, overlap, and covalency, we have been restricted to the simplest approximation using a point-charge lattice sum. Crystal-field coefficients can be conveniently expressed in the form¹⁴

$$A_{kq} = -e \frac{4\pi}{2k+1} \sum_i \frac{Q_i Y_{kq}^*(\theta_i, \phi_i)}{R_i^{k+1}} .$$

Apart from accurate structural data, an appropriate choice of ion charges is required for the numerical calculations. The bonding between the cation and the anionic complex XO_4 is mainly ionic in the scheelites, thus requiring the charges $+2e$ and $-2e$, respectively. The situation inside the tetrahedral oxocomplexes $(XO_4)^{2-}$ is more complex due to considerable covalency. Molecular-orbital calculations¹⁵ yielded effective oxygen charges Q_O of about $-0.75e$ for free molecular ions $(XO_4)^{2-}$. To avoid this uncertainty we have numerically calculated crystal-field coefficients as linear functions of effective oxygen charges. The complete results have already been published elsewhere.¹⁶ This method allows a proper assignment of charge magnitudes *a posteriori* when comparing this with experimental results.

The calculated crystal-field coefficients in relation to the effective oxygen charge reduced to a dimensionless variable Q_0 by the relation $Q_O = Q_0 e$ are plotted in Figs. 1 and 2. As the coefficient A_{44} depends also upon the angle ϕ_0 which marks the "magnetic" x axis, one cannot plot it in such a simple way. For a given ϕ_0 it may be obtained from the tabulated values.¹⁶

When looking for the mechanism which dominates the zero-field splitting of Mn^{2+} in scheelites, one has to remember the change of sign of D_0 when going from tungstates to molybdates. For this reason all processes yielding a quadratic dependence of D upon single crystal-field coefficients (such as the Watanabe¹⁷ and the Orbach-Das-Sharma² process) can be excluded. These two mechanisms, as well as the

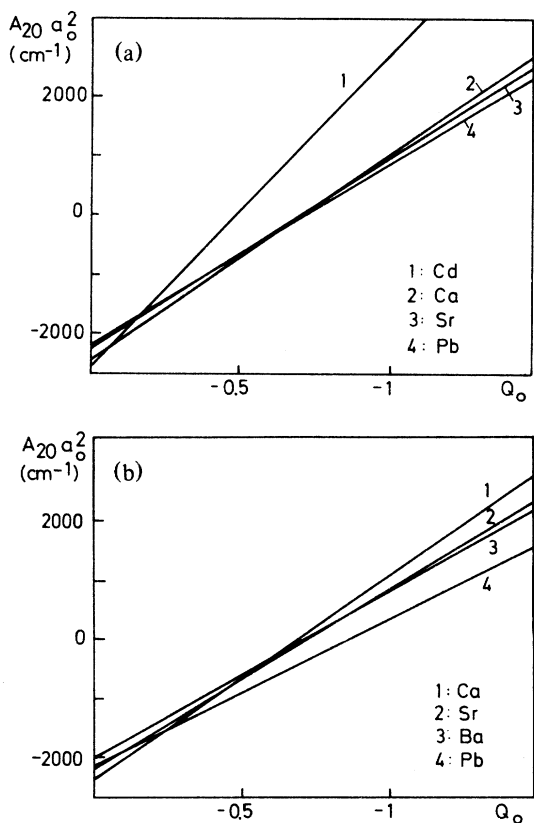


FIG. 1. (a) Molybdates: crystal-field coefficient A_{20} vs oxygen charge. (b) Tungstates: crystal-field coefficient A_{20} vs oxygen charge.

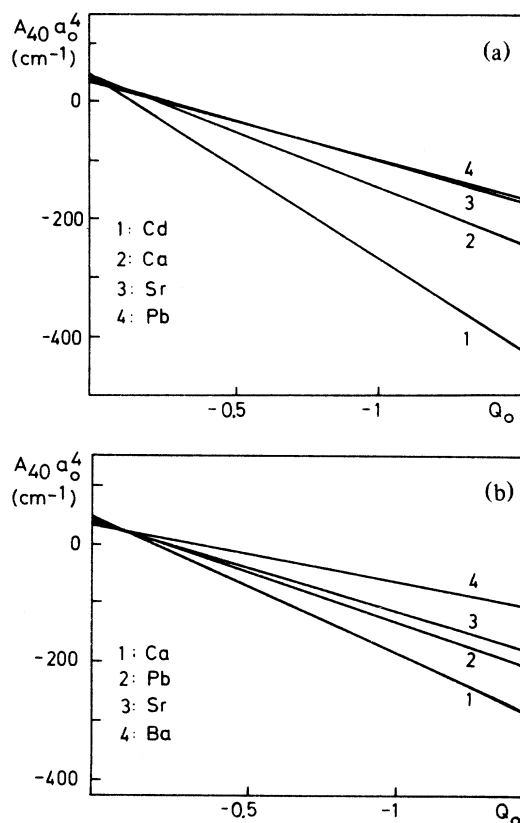


FIG. 2. (a) Molybdates: crystal-field coefficient A_{40} vs oxygen charge. (b) Tungstates: crystal-field coefficient A_{40} vs oxygen charge.

Pryce mechanism, have already been found to be of minor importance in the case of MnF_2 and ZnF_2 .² These authors concluded that the Blume-Orbach (BO) mechanism¹⁸ is the dominant contribution to the ground-state splitting of Mn^{2+} . In this process the 4L excited states are mixed by the cubic part of the crystal field, and the spin-orbit coupling produces a weak admixture of the resulting cubic-field eigenstates into the 6S ground state. This yields a zero-field parameter D_{BO} which is proportional to a linear combination of $n=4$ crystal-field parameters²:

$$D_{\text{BO}} = -B_4' \frac{\sqrt{5}}{36} \langle r^4 \rangle [\xi^2 P_{\alpha\gamma} (2p_{\alpha\alpha} - p_{\alpha\beta})]$$

Despite all uncertainty about quantities like p_{ij} , ξ , and $\langle r^4 \rangle$, a change of sign of D_{BO} can only be caused by the crystal-field parameter. According to our calculations the crystal-field coefficient in question does not change its sign within the range of reasonable oxygen charges when a tungstate and a molybdate with the same cation are compared. Consequently the Blume-Orbach mechanism seems to be less important to the ground-state splitting of Mn^{2+} in scheelites.

C. Relativistic effect

The application of relativistic wave functions in crystal-field theory proposed for the first time in 1955¹⁹ has been transferred to the 6S state of Mn^{2+} by van Heuvelen.²⁰ His calculation produces the result

$$D = \frac{3\xi A_{20} \langle b_2(11) \rangle}{125[E(^4P) - E(^6S)]}$$

So in this case the splitting parameter D is related to the second-order crystal-field coefficient.

An examination of the calculated A_{20} values¹⁶ plotted in Fig. 1 shows that a change of sign of this parameter and consequently of D for most of the scheelites in question occurs in the range of oxygen charges Q_o between $-0.70e$ and $-0.75e$. This result is very encouraging since molecular orbital (MO) calculations¹⁵ as well as an analysis²¹ of optical spectra in the system $\text{AXO}_4:\text{Yb}^{3+}$ show this to be apparently a very reasonable value for the oxygen charge. So an unconstrained explanation of the ground-state splitting of Mn^{2+} in scheelites seems to be possible using

TABLE III. Effective oxygen charges in scheelites (e).

Sample	CdMoO ₄	CaMoO ₄	SrMoO ₄	PbMoO ₄	CaWO ₄	SrWO ₄	PbWO ₄
Q_O	(-0.44)	-0.68	-0.68	-0.63	-0.84	-0.86	(-0.90)

the relativistic crystal field.

A value of $-0.0485a_0^2$ has been given²⁰ for $b_2(11)$ which is a linear combination of relativistic radial integrals. In a later revision of the theory Hagston and Lowther²² suggested that van Heuvelen's result be multiplied by a factor of 2 to 3. Also taking the uncertainty about the correct value of the spin-orbit-coupling constant and the energy levels into account, the rough evaluation

$$10^{-5}a_0^2 |A_{20}| \leq |D| \leq 4.6 \times 10^{-5}a_0^2 |A_{20}|$$

is obtained. For this reason we have chosen a mean proportionality factor and used the relation

$$D = -2.8 \times 10^{-5}a_0^2 A_{20}$$

for the numerical evaluation of our experimental data.

The A_{20} values obtained from the D_0 values given in Table II by this relation are then assigned proper oxygen charges. These are listed in Table III. In the case of CdMoO₄ and PbWO₄ we feel the results of this procedure should be disregarded. This is because the structural data of these compounds seem to be a little bit doubtful, and the calculations are rather sensitive to the fractional oxygen coordinates.

An inspection of the effective oxygen charges in the remaining five scheelites shows a characteristic charge difference of about $0.17e$ between tungstates and molybdates. We believe this to be caused by the different electronegativities χ of tungsten and molybdenum. As can be seen from Table IV the difference in χ is larger for the pair W-O than for Mo-O. This results in a more covalent character of the chemical bond inside the MoO₄ complexes, respectively, in larger oxygen charges in the tungstates. In addition the cation has also an influence. Cations with the same electronegativity (Ca, Sr) yield practically equal oxygen charges ($-0.68e$ in molybdates, $-0.85e$ in tungstates). Larger electronegativity

of the cation, as in the case of Pb, results in a smaller difference to the electronegativity of oxygen and thereby evidently in a reduction of the effective oxygen charge ($-0.63e$ in PbMoO₄).

This tendency can also be confirmed indirectly in the case of PbWO₄ and CdMoO₄ by the experimental values of D_0 . As one can see from Fig. 1, a reduction of the oxygen charge leads to a decrease in A_{20} and consequently to an increase in D_0 . Hence the sequence of experimental values for D_0 is in absolute accordance with the order of oxygen charges expected from the corresponding electronegativities.

Finally we will have a short look at the spin-Hamiltonian parameters of fourth order and especially at the b_4^0 values which have been determined for all samples. We have already mentioned that this parameter also reflects the characteristic difference between tungstates and molybdates, though only by the order of magnitude and not by a change of its sign. The results plotted in Fig. 2 are in accordance with these findings since all of the calculated A_{40} coefficients have the same sign if the absolute value of the oxygen charge exceeds $0.4e$. Using van Heuvelen's result for D as a basis we might tentatively assume a proportionality $b_4^0 \sim A_{40}$. Then one can explain the fact that the b_4^0 values are more negative in tungstates than in molybdates also by the existence of different oxygen charges in the two groups of compounds.

IV. CONCLUSION

All in all the experimental results on the ground-state splitting of Mn^{2+} in scheelites can be well understood in terms of the relativistic crystal-field contribution and simple assumptions on the nature of the chemical bond in these crystals. We hope to be able to improve this analysis further by getting experimental information about the crystal-field parameters from planned optical measurements.

TABLE IV. Electronegativities of some interesting elements.

Element	Ca	Sr	Ba	Cd	Pb	Mo	W	O
Electronegativity	1.0	1.0	0.9	1.7	1.8	1.8	1.7	3.5

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