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Spin Hamiltonian Parameters for Co^{2+} Ions in $PbMoO_4$ Crystal — Interplay between the *Fictitious* Spin $S' = 1/2$ and the *Effective* Spin $\tilde{S} = 3/2$

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The interplay between the *fictitious* spin $S' = 1/2$ and the *effective* spin $\tilde{S} = 3/2$ for $Co^{2+}(3d^7)$ ions is considered. The available experimental data on the Ze g'_i factors for the two Co^{2+} complexes in $PbMoO_4$ obtained using the *fictitious* "spin" $S' = 1/2$ description serve for determination of the Zeeman g_i factors corresponding to the *effective* spin $\tilde{S} = 3/2$. The second-rank zero-field splitting parameters D and E ($\tilde{S} = 3/2$) are also indirectly determined from the experimental EMR data by employing the formulas arising from projection of the $g_i(\tilde{S} = 3/2)$ factors onto the $g'_i(S' = 1/2)$ factors. The so-determined second-rank zero-field splitting parameters and $g_i(\tilde{S} = 3/2)$ factors will enable comparison with the respective quantities obtained in a subsequent paper using a combined modeling approach.

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1. Introduction

Two major descriptions of the ground state of $Co^{2+}(3d^7)$ ions with the electronic spin $S = 3/2$ in crystals have been used in literature, which represent different origin in terms of the sequence of the energy levels involved; for references, see, e.g. [1–6]. The ground state of Co^{2+} ($S = 3/2$) ions may described either by the effective spin $\tilde{S} = 3/2$ or in the case of very large zero-field splitting (ZFS) by the fictitious "spin" $S' = 1/2$. The latter "spin" (S') is associated with the lowest Kramers doublet within the effective spin $\tilde{S} = 3/2$ states and is often inappropriately named as the effective spin. The notions: effective spin $\tilde{S}$ and fictitious "spin" S' have been defined and their distinction clarified in the reviews [7, 8] and more recently in [9]. Survey of the feasible options for the origin of the Co^{2+} ground state with $\tilde{S} = 3/2$ and $S' = 1/2$ at sites with various coordination and symmetry requires a separate review and is beyond the scope of this paper.

The superposition model (SPM) analysis [10, 11] utilize the structural data for the host crystal as well as the distorted local environment around the dopant ions. Thus SPM calculations enable correlation of the spectroscopic and structural data. In general, the SPM analysis may be utilized for determination of the ZFS parameters (ZFSPs) [1–6]. Then, the SPM-predicted ZFSPs may be directly matched with the experimental ZFSPs measured by electron paramagnetic resonance (EPR). The SPM/ZFS approach enables reliable determination of the local structural distortions and feasible positions of the dopant ions in crystals, especially for the S-state transition-metal ions, like Fe^{3+} and Mn^{2+} [10, 11]. However, no suitable SPM parameters are available for Co^{2+} ions doped into the substitutional sites in $PbMoO_4$ crystal (Co^{2+}:$PbMoO_4$). Hence, we have recently started working out independent modeling of the ZFSPs and the Zeeman electronic (Ze) g_i factors for $Co^{2+}(S = 3/2)$ ions in $PbMoO_4$. These studies employ a combined approach based on the crystal field (CF), or equivalently ligand field (LF), theory [7–9] and SPM analysis to predict first the CF parameters (CFPs) for Co^{2+}:$PbMoO_4$. Subsequently, the SPM-predicted CFPs will be used as input for the CFA/MSH package [12, 13], which incorporates the CF analysis (CFA) and the microscopic spin Hamiltonian (MSH) modules. The combined SPM/CF+CFA/MSH approach, i.e. ZFSP modeling based on SPM analysis of the CFPs and subsequent application of the CFA/MSH package, enables modeling the optical energy levels and the SH parameters, i.e. ZFSPs and the Ze g_i factors. Various structural models need to be considered to predict reliably CFPs and ZFSPs for Co^{2+}:$PbMoO_4$.

This paper prepares grounds for modeling the CF parameters and SH ones for the two Co^{2+} complexes in $PbMoO_4$ [14, 15] in a follow-up paper [16]. The second-rank ZFSPs D and E and the Ze g_i factors are indirectly determined for the effective spin $\tilde{S} = 3/2$ from available experimental EMR data on the Ze g_i factors established for the fictitious "spin" $S' = 1/2$ [17–19]. For this purpose, we employ the formulae [17] arising from projection of the $g_i(\tilde{S} = 3/2)$ factors onto the $g_i(S' = 1/2)$ factors. The so-determined ZFSPs D and E and $g_i(\tilde{S} = 3/2)$ factors will enable comparison with the respective quantities obtained using the SPM/CF+CFA/MSH modeling approach in a subsequent paper [16].

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2. Spin Hamiltonian for fictitious spin $S' = 1/2$ and effective spin $\tilde{S} = 3/2$

Since the pertinent background for the SH theory is available in literature, we only provide a brief outline and references. Irrespective of the nature of the spin, for a paramagnetic spin $S = 1/2$ system with a nuclear spin I, like $Co^{2+}(S' = 1/2, I = 7/2$ — for the ^{59}Co isotope), EPR spectra may be described by a general (triclinic) SH consisting of the Ze electronic term and the hyperfine interaction term see, e.g. [1–9]:

$$H = \mu_B B \cdot g \cdot S + S \cdot A \cdot I. \quad (1)$$

Likewise, irrespective of the nature of the spin, for a paramagnetic spin $S = 3/2$ system, like $Co^{2+}(\tilde{S} = 3/2)$, only the 2nd-rank ZFS terms exist, which for orthorhombic and lower symmetry may be expressed in the principal axis system (PAS) of the 2nd-rank ZFS terms, i.e. the $\boldsymbol{D}$-tensor, as [1–9]:

$$H_{ZFS} = D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + E\left(S_x^2 - S_y^2\right), \quad (2)$$

where the conventional ZFSPs D (axial) and E (rhombic) are related to those in the Stevens notation as: $D = 3B_2^0 = b_2^0$, $E = B_2^2 = \frac{1}{3}b_2^2$ [7–9, 20]. For axial symmetry, e.g. tetragonal (C_{4h}, S_4) type II sites [21] existing in pure $PbMoO_4$, $E = 0$. The origin of the fictitious spin $S' = 1/2$ for Co^{2+}:$PbMoO_4$ is illustrated in Fig. 1.

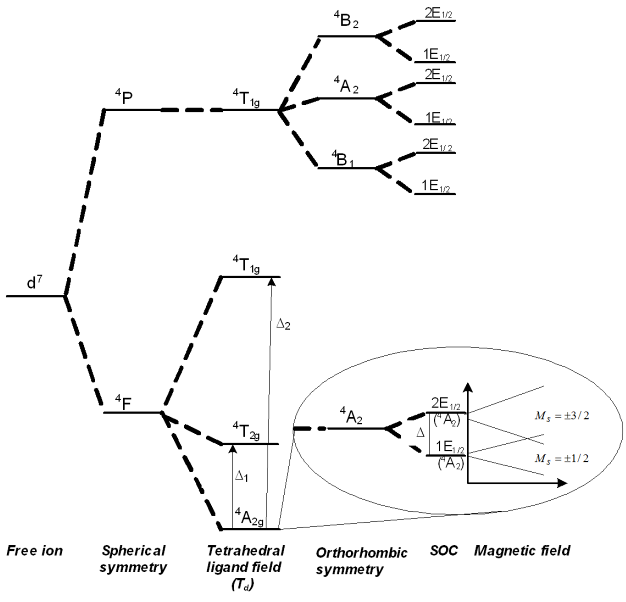

Fig. 1. Crystal-field energy levels diagram showing the origin of the fictitious spin $S' = 1/2$ from the effective spin $\tilde{S} = 3/2$ arising from the action of the spin–orbit coupling due to the large ZFS for the four-coordinated Co^{2+} ions in $PbMoO_4$.

3. Correlation between the Zeeman factors $g_i(S' = 1/2)$ and $g_i(\tilde{S} = 3/2)$

Analysis of EPR data [19] has revealed that Co^{2+} ions doped into $PbMoO_4$ may be characterized by the fictitious spin $S' = 1/2$ with the Ze g_i' factors listed in Table I. Concerning the orientation of the principal axes of the $\boldsymbol{g}$-tensor for the complexes $Co^{2+}(\alpha)$ with respect to the crystallographic axes $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$ in $PbMoO_4$ crystal, we follow the definitions outlined in [19, 22]. The results [19] correlate well with interpretations of earlier optical measurements [22], thus suggesting that Co^{2+} ions substitute at the Mo^{6+} tetrahedral sites. The g_i' values [19] are very close to the principal g_i' values determined for Co^{2+} in $PbWO_4$ crystals by Chen and Artman [17, 18]. Correlation between the experimental (or calculated) principal $\boldsymbol{g}$-tensor values: g_i' for the $S' = 1/2$ ground Kramers doublet and g_i for the $\tilde{S} = 3/2$ multiplet, may be achieved using the relations given in [17]:

$$\begin{cases} g_z' = g_z(C_2^2 - 2C_1^2), \\ g_x' = 2g_x(C_2^2 + \sqrt{3}C_1C_2), \\ g_y' = 2g_y(C_2^2 - \sqrt{3}C_1C_2), \\ C_1 = \sqrt{\frac{3E^2}{2D^2+6E^2+2D\sqrt{D^2+3E^2}}}, \\ C_2 = \sqrt{\frac{2D^2+3E^2+2D\sqrt{D^2+3E^2}}{2D^2+6E^2+2D\sqrt{D^2+3E^2}}}, \\ C_1^2 + C_2^2 = 1, \\ \Delta = 2\sqrt{D^2+3E^2}, \\ g_x \geq g_y, \end{cases} \quad (3)$$

where g_z', g_x', and g_y' are, in the terminology used in [17], the "apparent" $\boldsymbol{g}$-tensor components, i.e. for $Co^{2+}(S' = 1/2)$, whereas g_z, g_x and g_y are the three "intrinsic" principal $\boldsymbol{g}$-tensor values appropriate before the mixing of the spin states by D and E terms, i.e. for $Co^{2+}(\tilde{S} = 3/2)$. The relations in Eqs. (3) arise from projection of the $g_i(\tilde{S} = 3/2)$ factors onto the $g_i'(S' = 1/2)$ factors taken within the respective basis of states [17]. The parameter Δ in Eqs. (3) represents [17] the separation energy between the $M_s = \pm 1/2$ with $M_s = \pm 3/2$ states (see Fig. 1), i.e. the ZFS of the $\tilde{S} = 3/2$ multiplet [1–6]. From the temperature dependence of the spin–lattice relaxation rate between 10 and 20 K, assigned to an Orbach-type process, the value $\Delta = 83 \pm 7$ cm^{-1} was obtained for Co^{2+} in $PbWO_4$ crystal [17].

Comparison of the unit cell parameters [14, 15] of $PbWO_4$ and $PbMoO_4$ indicates their structural similarity. Hence, since the EPR spectra of Co-doped $PbWO_4$ and $PbMoO_4$ were attributed to Co^{2+} ions occupying tetrahedral W (or Mo) sites of S_4 symmetry in [17, 18], the value of Δ for Co^{2+} in both crystals may be expected to be comparable. Taking as input the experimental g_i' values for the two Co^{2+} complexes in $PbMoO_4$ [19] listed in Table I and the three values of Δ: 76, 83, 90 (in cm^{-1}) within the experimental uncertainty limits [17], we resolve Eqs. (3) numerically using the MathCad package.

Since Eqs. (3) are non-linear, several solutions may be obtained. A question arises concerning clear, unambiguous criteria for selection of the final solutions. The solutions listed in Table I have been selected using specific constraints, namely, (i) keeping the coefficients C_1 close to 0, while C_2 close to 1 which corresponds to nearly axial symmetry, (ii) keeping both coefficients real to ensure physically meaningful solutions, and (iii) adopting the starting values of g_i for fittings close to

2.0023, i.e. the free electron values, in accordance with expectations based on the MSH theory and experimental data [16, 23, 24] Hence, the final solutions (Table I) may be deemed as most sensible from the point of view CF and MSH theory as well as the observed experimental data for other similar Co^{2+} complexes. Taking into account the experimental uncertainty ±0.1 of the measured g'_i values of Co^{2+} ions in $PbMoO_4$ [19], the uncertainty of g_i values calculated using Eqs. (3) was determined by total differential method as ±0.1, whereas the uncertainty of the quantities C_1, C_2, D and E was determined using the relative percentage error as (±0.04%), (±0.002%), (±0.01%) and (±0.06%), respectively.

TABLE I

Experimental and calculated parameters for the Co^{2+} complexes in $PbMoO_4$ crystal (CN = 4).

Spin	Calculated (this work) $S = 3/2$						Expt. [19] $S' = 1/2$
Complex	(g_x, g_y, g_z)	D [cm^{-1}]	E [cm^{-1}]	C_1	C_2	Δ [cm^{-1}] [17]	(g'_x, g'_y, g'_z)
$Co^{2+}(\alpha)$	(2.84, 2.51, 1.99)	41.95	2.89	0.0606	0.9982	83	(6.26, 4.47, 1.97)
$Co^{2+}(\beta)$	(3.30, 1.79, 1.72)	41.05	3.53	0.0739	0.9973		(7.41, 3.10, 1.69)
$Co^{2+}(\alpha)$	(2.85, 2.49, 1.99)	44.70	3.00	0.0579	0.9983	90	
$Co^{2+}(\beta)$	(2.83, 2.58, 1.95)	41.05	10.64	0.2094	0.9778		
$Co^{2+}(\alpha)$	(2.84, 2.51, 1.99)	37.71	2.71	0.062	0.9981	76	
$Co^{2+}(\beta)$	(3.30, 1.79, 1.72)	37.58	3.26	0.0744	0.9972		
	Calculated [17]						Expt. [17]
Co^{2+}:$PbWO_4$	(2.82, 2.52, 2.10)	41.37	2.87	0.0598	0.9983	83	(6.20, 4.50, 2.07)

Irrespective of the g values used, the coefficient C_1 appears, in all cases considered here, to be very small as compared to C_2, which turns out to be very close to unity. This indicated that the ground doublet is predominantly the $M_s = \pm 1/2$ state with just a small admixture from the $M_s = \pm 3/2$ states due to the E term [17]. The ZFS parameters obtained by us for the complex $Co^{2+}(\alpha)$ and $Co^{2+}(\beta)$ (see Table I) are comparable in magnitude to the calculated ones reported in [17]. However, our results for the ZFSP D and that in [17] are large compared to those reported for Co^{2+} in crystals with tetrahedral site symmetry [17, 25–27]. A non-zero E-value indicates a small rhombic distortion of the Co^{2+} complexes. The so-obtained ZFSPs D and E (Table I) will serve for comparison with those predicted using the SPM/CF+CFA/MSH approach [16]. Preliminary results [16] indicate that a good agreement between the two sets of ZFSPs may be achieved. Hence, the combined approach, based on the SPM analysis of CFPs and followed by application of the CFA/MSH package, is suitable for prediction and modeling of the ZFS parameters for Co^{2+} complex α in $PbMoO_4$ crystal. Detailed results and analysis, including consideration of optical data, will be given in [16].

Concerning the principal g_i values determined in Table I, a literature survey reveals a problem with the relative magnitudes of the g_i components for $Co^{2+}(\tilde{S} = 3/2)$ ions. The obtained g_z values smaller than the free-electron $g_e = 2.0023$ seem somewhat controversial in view of recent findings indicating the opposite relation for $Co^{2+}(\tilde{S} = 3/2)$ ions at tetrahedral sites, e.g. $g_z = 2.240$ [28] and $g_z = 2.362$ [29]. On the other hand, the measured g'_i values for $Co^{2+}(S' = 1/2)$ ions indicate highly asymmetric $\boldsymbol{g}$-tensor and several cases of $g'_z < 2.0023$ have been reported, e.g. 1.60 [30] and 1.64 [31]. These values may be indicative of a highly distorted tetrahedral environment. The condition $g_z > g_e$ may be satisfied within the uncertainty of the determined g_i values: ±0.1, which may increase to ±0.20 if other experimental factors are taken into account. Nevertheless, in view of the above disparities, the present results require additional justification and may necessitate reconsideration of the procedure used. This is, however, beyond the scope of this preliminary paper. These pertinent aspects will be dealt with in [16]. Better understanding of the spectroscopic properties of Co^{2+} ($\tilde{S} = 3/2$) ions in $PbMoO_4$ may be achieved due to application of the SPM/CF+CFA/MSH approach [16]. This will enable independent model calculations of the g_i components for $Co^{2+}(\tilde{S} = 3/2)$ ions. Then a closer examination of the relationships between the relative values of the g_i components for Co^{2+} ions obtained by us as compared with those available in literature will be carried out [16]. The analogy between the EPR spectra for cobalt $Co^{2+}(\tilde{S} = 3/2)$ ions and those for chromium $Cr^{3+}(\tilde{S} = 3/2)$ ions, apart of the difference due to the presence of the hyperfine structure of Co^{2+} ions [32], will be also discussed.

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