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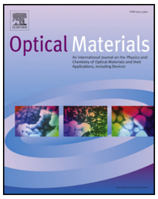

Modeling the zero-field splitting parameters and local structure of Co^{2+} ions doped into $PbMoO_4$ crystal based on crystal field approach and superposition model analysis

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ABSTRACT

Superposition model (SPM) analysis is employed for determination of the crystal field parameters (CFPs) for Co^{2+} ions doped into $PbMoO_4$ crystal. SPM calculations utilize structural data to model parameters spectroscopically measured for the dopant ions. The CFPs predicted by SPM assuming axial site symmetry serve as input for the CFA/MSH package, which incorporates the CF analysis (CFA) and the microscopic spin Hamiltonian (MSH) modules. This approach enables modeling of the optical energy levels as well as the axial SH parameters: zero-field splitting parameter (ZFSP) D and g_i factors: $g_{||}$ and $g_{\perp}$. The theoretical SH parameters are matched with the ones deduced from experimental electron magnetic resonance (EMR; EPR) data for $Co^{2+}(3\,d^7)$ ion using projection of g_i for the *effective* spin $\tilde{S} = \frac{3}{2}$ onto g_i' for the *fictitious* spin $S' = \frac{1}{2}$. Various structural models are considered to predict the CFPs and thus ZFSPs. The local distortion polar angles $\Delta\theta$ in the vicinity Co^{2+} ions in $PbMoO_4$ are obtained for tetrahedral (Mo^{6+}) and dodecahedral (Pb^{2+}) sites for two possible structural configurations, thus confirming the structural distortions induced by Co^{2+} doping. This enables discerning between Co^{2+} ions located at the Pb^{2+} sites and those at the Mo^{6+} sites. The experimental data available for one type of the two observed Co^{2+} complexes in $PbMoO_4$ are reanalyzed.

1. Introduction

The lead molybdate ($PbMoO_4$) crystals may easily accommodate rare-earth and transition-metal ion impurities at either Mo^{6+} four-coordinated tetrahedral sites (denoted TH) or Pb^{2+} eight-coordinated dodecahedral sites (denoted CD) [1,2]. Four crystallographically equivalent centers exist for both the Pb^{2+} and Mo^{6+} sites in the unit cell [1–4], each having two pairs of two magnetically inequivalent positions [1,2,4–7]. Hence, $PbMoO_4$ serves as a versatile optoelectronic material for various applications as acousto-optical deflectors, modulators, ion conductors, and effective low-temperature scintillators in nuclear instruments [8–12]. The spectroscopic and relaxation properties, and defect structures of the pure, rare-earth and transition-metal ions doped $PbMoO_4$ crystals have been extensively studied both theoretically and experimentally [4,6–17].

In view of potential applications we set on investigations of Co^{2+} ions doped into the substitutional sites in $PbMoO_4$ crystal (Co^{2+}:$PbMoO_4$). A combined approach based on the crystal field (CF), or equivalently ligand field (LF), theory [18–22] and superposition model (SPM) analysis [23–25] is employed to predict the CF parameters (CFPs) and subsequently the zero-field splitting (ZFS) parameters [26–30]. The SPM analysis utilizes the structural data for the host crystal as well as for the distorted local environment around the dopant ions and thus enables to correlate the spectroscopic and structural data. In principle, the SPM analysis can be employed directly for modeling the ZFS parameters (ZFSPs), albeit using different sets of model parameters then for SPM/CFP modeling. This route has turned out not feasible since no model parameters suitable for SPM/ZFS calculations have been found in literature. Hence, we have adopted a combined approach, whereby at the first stage the SPM analysis is utilized for determination of the CFPs and the local structural distortions for Co^{2+}:$PbMoO_4$ assuming axial site symmetry. At the second stage the SPM-predicted CFPs are used as input for the CFA/MSH package [31,32], which incorporates the CF analysis (CFA) and the microscopic

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spin Hamiltonian (MSH) [33–35] modules. Reliability of the SPM-predicted CFPs is then verified by comparison of available literature data on the CFPs the experimental and theoretical CF energy levels for Co^{2+} ions in related crystals. For Co^{2+} ions at axial sites, the CFA/MSH module [31,32] enables direct determination of the spin Hamiltonian (SH) parameters, i.e. ZFSP D and the Zeeman electronic (Ze) g_i factors: $g_{||}$ and $g_{\perp}$.

Appropriate axis systems are selected for the two possible sites substituted by Co^{2+} ions in the $PbMoO_4$ host crystal: (i) deformed dodecahedral 8-fold coordinated sites (Co^{2+} ions substituting for Pb^{2+} sites in the host crystal) and (ii) deformed tetrahedral 4-fold coordinated sites (Co^{2+} ions replacing Mo^{6+} ions). Spectroscopic studies [36,37] indicate that the axial S_4 symmetry determined based on the crystallographic data [1,2] for each site in pure $PbMoO_4$ is slightly lowered due to distortions induced by the dopant Co^{2+} ions (see, e.g. Refs. [17,38]). Consideration of the Co^{2+} ions at orthorhombic sites has not been attempted since the departure from axial symmetry appears to be small judging from structural and spectroscopic data [36,37]. Moreover, due to computational limitations of the CFA/MSH module [31,32], no information about the orthorhombic g_i factors can be extracted, whereas only one ZFS transition at zero magnetic field may be obtained, from which only the quantity $(D^2 + E^2)$ may be indirectly determined [26–30]. With the expected small value of the rhombic ZFSP E the axial symmetry approximation appears justified.

Our previous EMR study of Co^{2+}:$PbMoO_4$ single crystals correlated well with the interpretations of our earlier optical measurements and suggested that the Co^{2+} ions substitute at the Mo^{6+} tetrahedral sites [39,40]. The analysis of experimental EMR data on Co^{2+} ions doped into $PbMoO_4$ [39,40] and related $PbWO_4$ single crystals [36,37] has, however, been carried out based on an approximated SH, which corresponds to the fictitious spin $S' = 1/2$ approach (as defined in the reviews [33–35]). Thus the SH parameters (SHPs) obtained for Co^{2+} ions in EMR studies [36,37,39,40] comprise only the Ze g_i factors and cannot be directly compared with those obtained in the present calculations based on the effective spin $\tilde{S} = 3/2$ [33–35]. To enable such comparison the conversion formulas derived in Ref. [36], which relate the g_i factors corresponding to $\tilde{S} = 3/2$ and $S' = 1/2$, may be utilized. Illustrative preliminary results have been presented in Ref. [41].

In this paper the results of modeling the CF parameters and SH ones as well as the local structure parameters, based on the combined SPM/CFP + CFA/MSH approach, are presented in details for the two Co^{2+} complexes in $PbMoO_4$. The focus of the study [41] was on interplay between the *fictitious* spin $S' = ½$ and the *effective* spin $\tilde{S} = 3/2$ in spin Hamiltonian for Co^{2+} ions in $PbMoO_4$ crystal. The ZFSPs and g_i ($\tilde{S} = 3/2$) factors determined in Ref. [41] have enabled comparison with the respective quantities obtained in this paper using a combined modeling approach. Since the Co^{2+}($\tilde{S} = 3/2$) ions in $PbMoO_4$ exhibit large ZFS, Co^{2+}:$PbMoO_4$ and related systems may be potentially suitable for application as high-pressure probes for HMF-EMR studies [42–44]. Note that structural and electrical properties of $PbMoO_4$ have been studied under high pressure [3].

The present results may also guide our current investigations aimed at rational design of molecular nanomagnets (MNM) as well as computational modeling of their properties [35,45]. The MNM are formed by polynuclear or mononuclear clusters embedded in coordination complexes. The MNM systems nowadays encompass: the single-molecule magnets (SMM) [46], single-chain magnets (SCM) [47], and single-ion magnets (SIM) [48,49], based on various transition ions, including MNM based on Co^{2+}($\tilde{S} = 3/2$) ions. Due to their unique magnetic properties, e.g. phenomenon of macroscopic quantum tunneling of magnetization, as well as possible applications in high-density information storage and quantum computing [50], the MNM have become a subject of increased interest. Recently several MNM systems containing also Co^{2+} ions have been synthesized, some of them exhibiting very large ZFS; for references, see Refs. [46–49]. The present model calculations for systems with simpler crystal structure may be helpful in studies of more complicated ones. Hence, the proposed methodology and the sets of the model parameters determined here may be utilized for calculations of CFPs and ZFSPs for Co^{2+} ions at similar sites in SMM, SCM, or SIM systems.

The organization of the paper is as follows. In Section 2 the structural and spectroscopic characteristics of $PbMoO_4$ and Co^{2+}:$PbMoO_4$ crystals are briefly discussed. Section 3 presents methodology underlying this study, including SH and crystal field theory, and superposition model analysis. The results and discussion are given in Section 4. Summary and conclusions are provided in Section 5. The results may also be useful for interpretation of HMF-EMR data for Co^{2+} ($\tilde{S} = 3/2$) ions in structurally related complexes with axial symmetry.

2. Structural and spectroscopic characteristics

The $PbMoO_4$ crystal belongs to the scheelite-type crystal family with the tetragonal space group $I4_1/a$ and the point symmetry group C_{4h}^6 [1,2]. The $PbMoO_4$ unit cell consists of four atoms around the Pb^{2+} and Mo^{6+} ions, each site having S_4 point symmetry [1]. The Mo^{6+} ions are located at the centers of four regular O^{2-} tetrahedrons, forming four MoO_4 complexes, whereas the Pb^{2+} ions inside four dodecahedrons being surrounded by eight O^{2-}, forming four PbO_8 complexes [1,2]. For the Pb^{2+} as well as for the Mo^{6+} atoms there are four crystallographically equivalent sites, each two atoms have two magnetically inequivalent sites [1,2].

Two structural configurations consisting of two the unit cells have

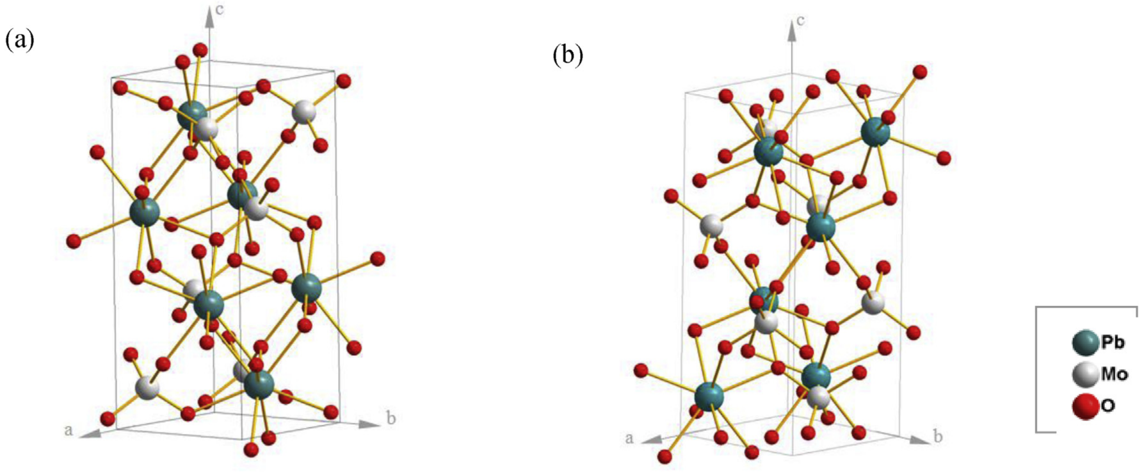

Fig. 1. Visualization of the $PbMoO_4$ unit cell based on the crystallographic data from: (a) Leciejewicz [1] and (b) Lugli et al. [51].