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Crystal field and magnetism with Wannier functions: Orthorhombic rare-earth manganites

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ABSTRACT

The crystal field parameters of seven R^{3+} ions (R=Pr, Nd, Sm, Eu, Gd, Tb, Dy) in $RMnO_3$ perovskites were calculated using the combination of the band structure and Wannier function calculations. Inserting the crystal field obtained in this way, in the atomic-like problem, which takes into account also the electron–electron correlation, the spin–orbit coupling and the Zeeman interaction, the splitting of the multiplets by the crystal field and the magnetic properties of the R^{3+} ions were obtained. The calculation is compared with the available experimental results.

1. Introduction

A novel theoretical approach has been recently used to calculate the crystal field parameters (CFP) in several rare-earth containing orthorhombic perovskites [1,2]. The method uses the density functional theory based band structure calculation, followed by a transformation of the Bloch to the Wannier basis and expansion of the local Hamiltonian in terms of the spherical tensor operators. The crystal field is subsequently inserted in an atomic-like program, which besides the crystal field accounts also for 4*f*–4*f* correlation, spin–orbit coupling and the Zeeman interaction. The calculated results are in a remarkable accord with the experiment: crystal field split multiplet levels agree within meV and also the magnetism is correctly described. In the well known laser materials R:$YAlO_3$ (R=Ce…Yb) an extensive set of optical data exists and the main goal of the calculation was to asses accuracy and robustness of the method. In the gallates and manganites the situation is more complex. These materials are not transparent and only a limited set of data is available. Reliable prediction of the crystal field is then vital for understanding their properties.

In this paper we treat the orthorhombic manganites $RMnO_3$ (R=Pr, Nd, Sm, Eu, Gd, Tb, Dy). These materials are similar to cobaltites and gallates, but there is an important difference: relatively strong Mn–Mn exchange interaction leads to a magnetic ordering with the critical temperature ~ 100 K. At low temperatures the exchange field polarizes the R states, the polarization is anisotropic making the analysis of magnetic properties complicated. For Kramers ions the dependence of the energies $E_i^\pm$ of the *i*-th Kramers doublet on the external magnetic field $\vec{B}$ may be written as

$$E_i^\pm(B) = E_i^\pm(0) \pm \frac{1}{2}\mu_B|\vec{B}|\,g(\vec{n}) - \frac{1}{2}\vec{B}\,\hat{\chi}^{vV}\vec{B}; \quad \vec{n} = \frac{\vec{B}}{|\vec{B}|}, \qquad (1)$$

where g is the effective *g*-factor and $\hat{\chi}^{vV}$ is the van Vleck susceptibility. The exchange energy is assumed to be part of the field independent $E_i^\pm(0)$. By measuring dependence of energy levels on the magnetic field the *g*-factor and $\hat{\chi}^{vV}$ may be thus determined. For non-Kramers ions the linear term is missing. Note, however, that for an antiferromagnetically ordered system the external field must be larger than the exchange field.

With exception of a single parameter, to be discussed below, the method is fully *ab initio* i.e. the only necessary inputs are the atomic composition and the crystal structure of the compound in question. This makes the method different from most of the earlier attempts to determine the crystal field of rare-earth ions (see Ref. [3] for a recent survey of a history of calculation the crystal field parameters in rare-earth compounds). An asset of the method is that once the local Hamiltonian is constructed, there is an unequivocal correspondence between its matrix elements and the crystal field parameters. This is important especially in the case of a low symmetry of the rare-earth site, where up to 27 parameters are needed to characterize fully the crystal field. In the semiempirical methods, as well as when the crystal field parameters are obtained by analyzing the optical experiments, the least squares fit is usually used. This, however, is difficult and often an ambiguous procedure.

The parameter Δ, on which the results depend, characterizes the hybridization between the rare-earth 4*f* states and the valence states of its oxygen ligands. In the 3*d* metal compounds the

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hybridization is in most cases a dominating source of the crystal field. For the Co:ZnO system Kuzian et al. [4] successfully reproduced the *g*-factors and the zero-field splitting, by treating the hopping between the cobalt 3*d* orbitals and the 2*p* states of the oxygen ligands as a perturbation to the charge-transfer term Δ_{pd}. The ideas and parametrization of Harrison [5] were used. Our treatment of the hybridization is analogical to that of Kuzian et al. and we briefly described it in [1]. The crystal field in the rare-earth oxides differs, however, from one of the 3*d* systems in that the Coulomb interaction prevails, though the contribution of the hybridization may also be significant.

The paper is organized as follows: the substance of the method and the details of calculation are described in Sections 2 and 3, respectively. The calculated crystal field parameters are presented in Section 4. In the same section the theoretical crystal field spectra are compared with the available experimental data deduced from the infrared spectra in high magnetic fields in Pr-, Nd- , Sm -, and Dy-compounds [6–10] and with the low temperature magnetic data [11]. In Section 5. the limitations of the method are briefly discussed and a possibility to apply it to the intermetallic compounds is indicated.

2. Methods

The effective Hamiltonian operating on the 4*f* states can be written as

$$\hat{H}_{eff} = \hat{H}_A + \hat{H}_Z + \hat{H}_{CF}, \qquad (2)$$

where $\hat{H}_A$ is the spherically symmetric free ion, atomic-like Hamiltonian, $\hat{H}_Z$ corresponds to the Zeeman interaction and $\hat{H}_{CF}$ is the crystal field term. In the Wybourne notation [12] $\hat{H}_{CF}$ has the form

$$\hat{H}_{CF} = \sum_{k=0}^{k_{max}} \sum_{q=-k}^{k} B_q^{(k)} \hat{C}_q^{(k)}, \qquad (3)$$

where $\hat{C}_q^{(k)}$ is a spherical tensor operator of rank *k* acting on the 4*f* electrons of the R ion, for which k_{max} is equal to six. The coefficients $B_q^{(k)}$ are the crystal field parameters. Hermiticity of $\hat{H}_{CF}$ requires that $(B_{-q}^k)^* = (-1)^q B_q^k$. The details of $\hat{H}_A$ are given e.g. in Ref. [13]. In the manganites with the orthorhombic *Pbnm* structure the R cations are located on sites of C_s point symmetry, which leads to nine independent crystal field parameters, three are real ($k=2$, 4, 6, $q=0$) and six complex ($k=2$, 4, 6; $q=2,4,6$; $q \le k$).

Calculation of the crystal field parameters consists of four steps:

1. Standard selfconsistent band calculation with 4*f* states included in the core. The result of this step is the crystal potential, which is subsequently used in the next step.
2. The 4*f* and oxygen 2*p*, 2*s* states are treated as the valence states in a nonselfconsistent calculation, all other states are moved away using the orbital shift operator. Relative position of 4*f* and oxygen states is adjusted using the 'hybridization' parameter Δ (the only parameter of method).
3. The 4*f* band states are transformed to Wannier basis using the wien2wannier [14] and wannier90 [15] packages.
4. Local 4*f* Hamiltonian in the Wannier basis is extracted and expanded in series of spherical tensor operators. The coefficients of expansion are the crystal field parameters.

With the crystal field parameters in hand we use the modified 'lanthanide' package [16] to solve the eigenvalue problem for Hamiltonian (1). The splitting of multiplets by the crystal field is then readily obtained and the dependence of energy levels on the direction and magnitude of the external magnetic field yields the $\hat{g}$ tensor. A detailed description of the analysis may be found in [1,2].

3. Details of calculation

For the band structure calculations (steps 1 and 2 in the previous section) the WIEN2k package [17] was used. For the exchange-correlation functional the generalized-gradient approximation form [18] was adopted. The experimental crystal structure of orthorhombic manganites was taken from [19,20,22,21]. The eigenvalue problem was solved in 60 points of the irreducible Brillouin zone and the number of basis functions was $\sim$ 2500 (corresponding to parameter $RK_{max}=7$). The calculations were non-spin-polarized. The atomic radii of R, Mn and oxygen were 2.3, 1.9 and 1.6 a.u., respectively.

The magnitude of the hybridization parameter Δ, needed in the second step, was fixed at 8.2 eV (0.6 Ry). This value led to a very good agreement of calculated and experimental rare-earth multiplet splitting and magnetism in the orthorhombic aluminates, gallates and cobaltites [1,2].

The 'lanthanide' program needs as input the parameters of the free ion Hamiltonian $\hat{H}_A$. The multiplet splitting and magnetism of rare-earth ions depend only slightly on their values, though there may be exceptions when the difference of the free ion multiplet energies is small. Carnall et al. [23] determined the parameters of $\hat{H}_A$ for all R^{3+} ions in LaF_3 by carefully fitting the optical absorption spectra and we adopted them when calculated the results given below.

4. Results

4.1. Crystal field parameters

The unit cell of the orthorhombic manganites contains two crystallographically inequivalent rare-earth sites with the local symmetry C_s. The crystal field parameters are referred to the orthorhombic axes *a*, *b*, *c* (in a *Pbnm* setting). The reader is referred to Appendix A in [2] for a detailed description of the crystal structure. The nonzero independent parameters of the crystal field in $RMnO_3$ for R=Pr, Nd, Sm, Eu, Gd, Tb and Dy are collected in Tables 1 (real part) and 2 (imaginary part).

In Fig. 1 the absolute value $|B_q^k|$ of the crystal field parameters is displayed as a function of the number of 4*f* electrons. It is seen that the dependencies are smooth, the exception being $TbMnO_3$. We found that this is connected with the fact that $TbMnO_3$ structure [22] falls out of the structures for other manganites considered [19–21]. When instead of $TbMnO_3$ experimental structure the structure interpolated from $GdMnO_3$ and $DyMnO_3$ is taken, the dependence is smoothed (broken line in Fig. 1).

4.2. Comparison with experiment

When detecting experimentally the energy levels of the rare-earth ions, often encountered problem is that not all the levels are observed and it is then usually ambiguous to assign experimental to calculated levels. In the present context it concerns primarily the $^3H_6$ multiplet of Pr^{3+} ion and, to a lesser extent, the $^6H_{13/2}$ multiplet of Dy^{3+} ion. In these cases our assignment is only tentative, based on minimizing the difference of experiment and theory.

When comparing the calculated and experimental splitting of the multiplets by the crystal field, the lowest multiplet level as measured in the experiment was shifted so that it coincides with the calculated one. In this way the deviations caused by the