Crystalline and magnetism of Pr$^{3+}$ and Nd$^{3+}$ ions in orthorhombic perovskites

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Abstract

Fifteen parameters characterizing the crystal field of rare-earth ions in the RMO$_3$ perovskites (R = Pr, Nd, M = Ga, Co) are calculated using a first-principles electronic structure and the Wannier projection. The method contains a single adjustable parameter that characterizes the hybridization of R(4f) states with the states of oxygen ligands. Subsequently the energy levels and magnetic moments of the trivalent R ion are determined by diagonalization of an effective Hamiltonian which, besides the crystal field, contains the 4f electron–electron repulsion, spin–orbit coupling and interaction with magnetic field. In the Ga compounds the energy levels of the ground multiplet agree within a few meV with those determined experimentally by other authors. For all four compounds in question the temperature dependence of magnetic susceptibility is measured on polycrystalline samples and compared with the results of calculation. For NdGaO$_3$ the theory is also compared with the magnetic measurements on a single crystal presented by Luis et al (1998 Phys. Rev. B 58 798). Good agreement between the experiment and theory is found.

(Some figures may appear in colour only in the online journal)

1. Introduction

The rare-earth elements can be naturally incorporated in the crystal structures of many important groups of materials such as cuprates, manganites, or cobaltites, to name a few. While their s, p, and d electrons are involved in the bonding, the 4f orbitals are in many cases only weakly coupled to the rest of the crystal. This makes them a potential local probe, able to detect internal exchange fields. However, for the rare-earth ions to serve this purpose, knowing their response to the external field is a necessity. At temperatures well above the Kondo temperature the physics of the 4f electrons can be captured by an effective atomic Hamiltonian, in which the crystalline environment is described by a set of crystal-field parameters (CFPs).

To determine the CFPs experimentally the optical f–f transitions may be used to map out the individual crystal-field split multiplet levels [1, 2]. This approach suffers from several limitations. For example, polarization analysis is required to orient the crystal field with respect to the crystal axes, or non-dipole transitions are necessary for the R ion in a centrosymmetric position. Most importantly the optical methods are not applicable in metals where the f–f transitions are hidden by the optical response of the free carriers. Therefore theoretical determination of CFPs is of great importance, and there have been numerous attempts to calculate them. Using the \textit{ab initio} methods to this end is challenging, the most difficult problem being the spurious on-site interaction of the f electrons with the nonspherical potential they themselves create (self-interaction). Several ways to remove the effect of self-interaction on the crystal field were suggested [3–6], the results, however, suffered from other approximations, such as neglect of the hybridization of the f states with other valence orbitals. An overview of both the semiempirical and the \textit{ab initio} methods of CFP calculation can be found in [7].

Recently, some of us have developed a method to compute CFPs by expanding the local Hamiltonian expressed in the basis of Wannier functions into a series of spherical tensor operators [7, 8]. The method does not suffer from the f electron self-interaction and the hybridization is accounted for. It was tested on thirteen orthorhombic aluminates, R:YAlO$_3$ (R = Ce, Pr . . . Yb) and on TbAlO$_3$. For Nd:YAlO$_3$, Er:YAlO$_3$ and TbAlO$_3$, for which an extensive set of optical data exists, we compared the calculated energy levels of the R$^{3+}$ ion with the experimental ones to get agreement to within

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a few meV, which to our best knowledge was never achieved before.

In this paper we study the rare-earth gallates NdGaO$_3$ and PrGaO$_3$ and cobaltites NdCoO$_3$ and PrCoO$_3$, for which optical f–f spectra are not available. Besides the multiplet spectra, which we compare to the inelastic neutron scattering data for NdGaO$_3$ [9] and PrGaO$_3$ [10], we focus on the magnetic response of R ions and calculate the anisotropic g-factors and van Vleck susceptibilities. These are compared to the experimental data for NdGaO$_3$ monocrystal [11] and to the susceptibility on polycrystals of all four compounds, which was measured as part of this work. We find an excellent match between the theoretical and experimental susceptibility calculated for NdGaO$_3$, while the polycrystal averaged susceptibility compares well to the experimental data for NdGaO$_3$ and PrCoO$_3$.

The paper is organized as follows: in section 2 the effective Hamiltonian method and the way the crystal field is calculated are briefly summarized, as well as the way to determine the magnetic moments. In section 3 the experimental and theoretical results and their comparison are presented. In section 5 the results are discussed, followed by the conclusions in section 6.

2. Methods

2.1. Effective Hamiltonian

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

\[ \hat{H}_{\text{eff}} = \hat{H}_A + \hat{H}_Z + \hat{H}_{\text{CF}}, \]

(1)

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

\[ \hat{H}_{\text{CF}} = \sum_{k=0}^{k_{\text{max}}} \sum_{q=-k}^{k} B_{q}^{(k)} \hat{C}_{q}^{(k)}, \]

(2)

where \( \hat{C}_{q}^{(k)} \) is a spherical tensor operator of rank \( k \) acting on the 4f electrons of the R ion, for which \( k_{\text{max}} \) is equal to six. The coefficients \( B_{q}^{(k)} \) are the crystal-field parameters. Hermiticity of \( \hat{H}_{\text{CF}} \) requires that \( (B_{q}^{(k)})^* = (-1)^q B_{-q}^{(k)} \). The details of \( \hat{H}_A \) are given, e.g., in [13]. In the gallates and cobaltites with the orthorhombic Pbnm structure (see appendix A), the R cations are located on sites of C$_3$ point symmetry, which leads to nine independent crystal-field parameters; three are real (\( k = 2, 4, 6 \)) and six complex (\( k = 2, 4, 6; q = 2, 4, 6; q \leq k \)).

2.2. Calculation of crystal-field parameters

The procedure to calculate the crystal-field parameters may be divided into four steps.

1. The electronic structure of the material is calculated with the 4f orbitals treated as the core states, which feel and feed back a spherically symmetrical potential and density respectively. Here we use the density functional based WIEN2k package [14]. The calculation is non-spin-polarized, which leads to the spin independent CFPs. The selfconsistent procedure was stopped when the change of the total energy was smaller than 0.000 05 Ryd. The eigenvalue problem was solved in four points of the irreducible Brillouin zone and the number of basis functions was \( \sim 9200 \) (corresponding to parameter \( RK_{\text{max}} = 6.13 \)).

2. The eigenvalue problem is solved with the potential determined in the first step. The 4f orbitals are treated as the valence states, but only 2s and 2p states of oxygen are allowed to hybridize with them. Mixing of 4f with other than oxygen states is prevented by shifting these states to a high energy, using an orbital potential [8]. The charge transfer energy between 4f and oxygen states, which is not correctly described by any local or semilocal density functional method, is adjusted by shifting the oxygen states by energy \( \Delta \)—to this end an orbitally dependent potential is used. Although \( \Delta \) is an adjustable parameter in the present calculations, its value was fixed to \(-0.6\) Ryd (\(-8.2\) eV). The dependence of CFPs on \( \Delta \) and the physics behind it is discussed by Novák et al [8].

3. The Hamiltonian of the 4f band is expressed in the Wannier basis and its on-site part \( \hat{H}_{\text{CF}} \) is extracted. For this step the WIEN2WANNIER [15] and the WANNIER90 [16] programs are used.

4. The local Hamiltonian is expanded in the spherical tensor operators using a standard linear algebra program. The expansion coefficients are the CFPs.

2.3. Electronic structure, magnetic moments and susceptibility of rare-earth ions

To find the eigenvalues of \( \hat{H}_{\text{eff}} \) a modified ‘LANTHANIDE’ program [17] was used. The atomic parameters of \( \hat{H}_A \) are only weakly material dependent and we used the values determined by Carnall et al [18] for R$^{3+}$ ions in LaF$_3$.

The spectrum of the free Pr$^{3+}$ ion (electron configuration 4f$^3$) contains three \( \{L, S, J\} \) multiplets, the lowest one being \( ^3\!H_4 \) (\( J = 4 \)). The 4f$^3$ configuration of the Nd$^{3+}$ ion leads to four multiplets with the \( ^4\!I_{9/2} \) ground multiplet. The crystal field of the \( C_3 \) symmetry splits the Pr$^{3+}$ multiplets into 91 orbital singlets, while there are 182 Kramers doublet states originating from the multiplets of Nd$^{3+}$. The energies of Kramers doublets depend on the magnetic field as

\[ \varepsilon_{\pm} = \varepsilon(0) \pm \frac{1}{2} \frac{\mu B}{|B|} g(n) \tilde{n} - \frac{1}{2} \tilde{\chi} \tilde{B}, \quad \tilde{n} = \frac{\tilde{B}}{|B|}, \]

(3)

where \( \varepsilon(0) \) is the energy in zero field, \( g \) is the effective g-factor and \( \tilde{\chi} \tilde{B} \) is the van Vleck susceptibility. The g-factor depends
on the direction of the external magnetic field $\vec{B}/|\vec{B}| = (\partial_x, \partial_y, \partial_z)$ as given by
\[
g = \sqrt{\frac{g_x^2 \partial_x^2 + g_y^2 \partial_y^2 + g_z^2 \partial_z^2}{}}.
\]
(4)

Keeping with tradition we call $g_x$, $g_y$ and $g_z$ principal components of the $\hat{g}$-tensor, despite the fact that not $\hat{g}$ but $\hat{G} = \hat{g}\hat{g}$ is the true tensor, as discussed, e.g., by Abragam and Bleaney [19]. The situation is briefly clarified in appendix B. For the non-Kramers Pr$^{3+}$ ion linear term in $B$ is missing, leading to a quadratic dependence of energy on the magnetic field.

To determine $\hat{g}$ and $\hat{\chi}^{\text{VV}}$ tensors the eigenenergies $\varepsilon_i$ were calculated in an external magnetic field and expanded to the second power of $B$. The $\alpha$ component of the magnetic moment (in Bohr magnetons) of the eigenstate $i$ is given by the field derivative of its eigenenergy,
\[
m_i^{(\alpha)} = -\frac{\partial \varepsilon_i^{(\alpha)}}{\partial B_\alpha}.
\]

The low local symmetry admits a nondiagonal $\hat{g}$ and $\hat{\chi}^{\text{VV}}$ component $g_{ab}$ and $\chi_{ab}$ [18]. In order to determine the magnetic moment and susceptibility of a polycrystal the canonical form of the $\hat{g}$-tensor is needed. The principal $z$ axis of both tensors is parallel to the orthorhombic $c$ axis, while for the two inequivalent R sites the axis $x$ makes an angle $\pm\alpha_x$ and $\pm\alpha_y$ with the orthorhombic $a$ axis. To determine the canonical form of the tensors the $\varepsilon_i(B)$ dependence was calculated with the external field parallel to the orthorhombic axes and to the direction $\alpha$ which lies in the $c$-plane and makes angle $\pi/4$ with the orthorhombic $a$ axis. From these four quantities the canonical form of the tensor $\hat{g}$ may be obtained from
\[
\begin{align*}
\alpha_x &= \frac{1}{2} \arctg \frac{2g_{aa} - g_{bb}^2}{8g_{ab}^2 - 2g_{aa}^2 - 2g_{bb}^2}, \\
g_x &= \sqrt{\frac{g_{aa}^2 + g_{bb}^2}{2} + \frac{g_{aa}^2 - g_{bb}^2}{2 \cos(2\alpha_x)}}, \\
g_y &= \sqrt{\frac{g_{aa}^2 + g_{bb}^2}{2} - \frac{g_{aa}^2 - g_{bb}^2}{2 \cos(2\alpha_x)}}, \\
g_z &= g_{cc},
\end{align*}
\]
where the index of eigenstate was omitted. Analogous relations hold also for the susceptibility tensor—it is only necessary to replace the squares of the $\hat{g}$-tensor components by the components of $\hat{\chi}^{\text{VV}}$. To obtain the $g$-factor and the susceptibility of a polycrystal, averaging over the polar and azimuthal angles was performed. The temperature dependence of the R magnetic moment was calculated using the Boltzmann statistics,
\[
M^{(\alpha)}(T) = \sum_i m_i^{(\alpha)} \exp(-\varepsilon_i^{(\alpha)}/kT)/\sum_i \exp(-\varepsilon_i^{(\alpha)}/kT),
\]
where $k$ is the Boltzmann constant and $\alpha$ denotes the direction of the external magnetic field.

3. Experimental details

The magnetic measurements were performed on polycrystalline samples of NdGaO$_3$, PrGaO$_3$, NdCoO$_3$ and PrCoO$_3$ prepared by a standard ceramic method. The study was carried out using a SQUID magnetometer MPMS-XL (Quantum Design) and included DC susceptibility measured over the temperature range of 2–300 K in an applied field of 1 T. The observed data reflect the Curie and/or van Vleck paramagnetism of the rare earths, which is valid not only for the gallates but also, at least below ~150–200 K, for the cobaltites, since Co$^{3+}$ ions are in a non-magnetic low-spin state and their contribution to the susceptibility is negligible.

An onset of the antiferromagnetic ordering of Nd$^{3+}$ moments was detected by $\lambda$-peak in the specific heat experiments, giving $T_N = 1.0$ K for NdGaO$_3$ and $T_N = 1.25$ K for NdCoO$_3$, which is in agreement with earlier single crystal results [11, 20–22].

4. Results

4.1. Energy levels

Values of the nine nonzero CFPs calculated as described above are shown in appendix C. The $^4\text{I}_{9/2}$ ground multiplet of the free Nd$^{3+}$ ion is split in the $C_3$ crystal field into five Kramers doublets. Their energies for NdGaO$_3$ calculated with the CFPs from table C.1 and atomic parameters of Carnall et al. [18] are shown in figure 1. In [9] the energies of these doublets in NdGaO$_3$ were determined using inelastic neutron scattering and an attempt was made to interpret the experiment using the crystal-field Hamiltonian. Unfortunately the CFP calculation was based on questionable assumptions, it contained several fitting parameters and, as pointed out by Rudowicz and Qin [24], inconsistent notation was used. Our results, based on the new set of CFPs, agree very well with the experimental data as shown in figure 1.

The same authors applied inelastic neutron scattering to study also PrGaO$_3$ [10]. The ground state $^3\text{H}_4$ multiplet
of the Pr$^{3+}$ ion is split by crystal field into nine singlets; only six of the excited singlets were detected experimentally, however. The analysis then poses a problem of identifying the undetected singlets. Podlesnyak et al [10] decided that the sixth and the ninth singlet went undetected. The analysis suffers from the same problems as for NdGaO$_3$[24], however. In figure 2 we compare our calculations with two possible assignments of experimental data. The difference between theory and experiment is characterized by the mean square deviation
\[
\sigma = \sqrt{\frac{\sum_{j=1}^{n_{\text{exp}}} (E_j,_{\text{exp}} - E_j,_{\text{calc}})^2}{n_{\text{exp}}}}.
\]
Selecting the fifth and the seventh singlets undetected (denoted exp. A) leads to \(\sigma = 4.24 \text{ meV}\), in better agreement with the experiment than the choice of Podlesnyak et al (exp. B, \(\sigma = 10.34 \text{ meV}\)).

There is no experimental information on energy levels of R$^{3+}$ ions in the cobaltites. The present calculation indicates that the levels (figure 3) are not far from the levels in the gallates.

### 4.2. Magnetic moments and susceptibility

To fully characterize the magnetism of the Nd$^{3+}$ ion, eight quantities for each eigenstate are needed: three components of the \(\hat{g}\) and \(\hat{\chi}\) tensors along the orthorhombic axes and one component along the \(\omega\) direction intersecting the angle between \(a\) and \(b\). In the case of the non-Kramers Pr$^{3+}$ ion, four components of \(\chi^{\text{VV}}\) tensor are sufficient. For NdCoO$_3$, PrGaO$_3$ and PrCoO$_3$ these quantities are collected in appendix B. The data for NdGaO$_3$ are shown in table 1 and for the ground doublet they are compared to experimental data of Luis et al [11]. These authors measured the AC magnetic susceptibility of a NdGaO$_3$ single crystal along the three orthorhombic axes in the temperature range 0.07 K < \(T\) < 50 K in which only the lowest Kramers doublet is appreciably populated. The results showed that the Nd moments order antiferromagnetically at \(T_N \sim 1 \text{ K}\). By fitting the experimental results in the temperature range 5–50 K Luis et al [11] obtained the data denoted as ‘exp.’ in table 1.

The anisotropy of the magnetic moment is demonstrated in figure 4, in which the angular dependence of the ground state magnetic moment. External magnetic field 9 T is in the \(c\) plane, \(\Phi = 0^\circ\) and \(\Phi = 90^\circ\) correspond to \(a\) and \(b\) axes, respectively.
Table 1. \( \text{Nd}^{3+} \) ion in \( \text{NdGaO}_3 \). Energy of five Kramers doublets originating from the \( ^4I_{9/2} \) multiplet \( \hat{g} \) and \( \hat{\chi}^{\text{VV}} \) tensor components along the orthorhombic axes and \( \omega \) direction. \( \chi^{\text{VV}} \) is units of \( \mu_B T^{-1} \). The experimental values were determined by Luis et al [11] and they refer to the ground doublet.

| Doublet | \( \varepsilon(0) \) (meV) | \( g_{aa} \) | \( g_{bb} \) | \( g_{cc} \) | \( g_{\omega} \) | \( \chi_{aa}^{\text{VV}} \) | \( \chi_{bb}^{\text{VV}} \) | \( \chi_{cc}^{\text{VV}} \) | \( \chi_{\omega}^{\text{VV}} \) |
|---------|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1       | 0.00                | 1.998 | 2.735 | 2.576 | 1.907 | 0.0215 | 0.0125 | 0.0116 | 0.0043 |
| Exp.    | 1                   | 0.018(1) | 0.012(1) | 0.008(1) |
| 2       | 10.90               | 2.671 | 2.296 | 0.974 | 2.048 | -0.0109 | 0.0012 | 0.0075 | 0.0129 |
| 3       | 22.77               | 2.883 | 1.397 | 2.965 | 2.981 | 0.0000 | -0.0006 | -0.0068 | -0.0068 |
| 4       | 55.09               | 3.271 | 4.212 | 1.165 | 5.262 | -0.0002 | -0.0038 | -0.0009 | -0.0021 |
| 5       | 66.61               | 2.347 | 1.662 | 3.816 | 1.437 | -0.0084 | -0.0072 | -0.0093 | -0.0064 |

\( \alpha_{\text{VV}} = -35.2^\circ \). Let us note that these values are orders of magnitude larger than the isotropic van Vleck susceptibility of octahedrally coordinated low-spin \( \text{Co}^{3+} \), \( \sim 0.0001 \mu_B T^{-1} \) (\( \sim 0.0002 \text{ emu mol}^{-1} \text{ Oe}^{-1} \)).

In figures 5–8 the calculated temperature dependences of the inverse susceptibilities in polycrystalline samples are presented together with the experimental dependence for the four RMO\(_3\) compounds.

5. Discussion

In RGaO\(_3\) polycrystals both the experimental and calculated inverse magnetic susceptibilities are linear in temperature starting from \( \sim 30 \text{ K} \) and \( \sim 120 \text{ K} \) for \( R = \text{Pr} \) and \( \text{Nd} \), respectively. Deviation from the Curie-like behavior, observed above \( \sim 220 \text{ K} \) for \( \text{NdCoO}_3 \) (figure 6) and above \( \sim 150 \text{ K} \) for \( \text{PrCoO}_3 \) (figure 8), is related to the existence of the paramagnetic high-spin states of Co\(^{3+}\), lying close above the non-magnetic low-spin ground state. The corresponding
contributions to the magnetic susceptibility can be ascribed to the thermal excitation from the low-spin to the high-spin state [25, 26]. To obtain the Curie-like behavior shown in figures 6 and 8 as ‘experiment’ the excited states of Co$^{3+}$ were assumed to lie at 130 meV and 95 meV for NdCoO$_3$ and PrCoO$_3$, respectively.

There is a weak interaction (superexchange and classical dipolar) between the Nd$^{3+}$ moments, which leads to the C$_2$-type antiferromagnetic ordering at the temperature $T_N \sim$ 1 K [11]. At low temperatures the magnetism of NdMO$_3$ is modified by the interaction also above $T_N$. Using the mean-field approximation it would be straightforward to include the interaction in our scheme. The corresponding correction to the magnetic susceptibility decreases rapidly with increasing temperature and it becomes insignificant above 40 K. The study of magnetism of the RMO$_3$ compounds at low temperatures is in progress and will be the subject of a separate publication.

There are several approximations involved in the calculation of the CFPs discussed in [8]. Nevertheless, given that a single adjustable parameter is used, the agreement between the theory and experiment is very good. In particular, the results obtained for energy levels in PrGaO$_3$ (figure 2) indicate strongly that the two levels undetected by the neutron experiment [10] were misidentified previously [10]. Especially gratifying is the agreement of the van Vleck susceptibility $\chi^v$ in NdGaO$_3$ (table 1). Note that $\chi^v$ was introduced by Luis et al [11] to fit the susceptibility data in the vicinity of the Néel temperature. The agreement thus provides theoretical justification of the analysis of experimental data.

In this paper we documented that the method is well applicable to the trivalent rare-earth ions in oxides. There are two items which limit the application to other systems with strongly correlated electrons:

- The hybridization of the correlated electrons with other valence electrons must be weak, as it is not accounted for in a self-consistent way.
- The self-interaction of the correlated electrons must be avoided. This is difficult in systems in which these electrons are significantly more delocalized compared to the 4f electrons in oxides. The problem is that the delocalized electrons cannot be treated as the core electrons (see the first step of section 2.2).

Despite these limitations we believe that application to a wide class of the rare-earth compounds is possible. In particular the relatively successful attempt to calculate CFPs in the RCoO$_3$ system [3] indicates that good candidates are the intermetallic rare-earth compounds (in the method suggested in [3] the hybridization of the 4f states is disregarded entirely).

To summarize, there are two essential steps in the present approach: (i) construction of the effective model, and (ii) solution of the effective model. The main limitation involved in step (i) is the treatment of self-interaction. Step (ii) assumes a weak hybridization to the ligands, which limits the materials accessible with this approach. However, the Wannier function technique can without changes be applied to construct more extensive models, which include the ligand states explicitly. Obviously the solution of such models is more demanding and the link between the measurable quantities and the crystal-field parameters is less direct, both in the theory and interpretation of experiments.

6. Conclusions

We have calculated complete sets of crystal-field parameters for the rare-earth ions in NdGaO$_3$, PrGaO$_3$, NdCoO$_3$ and PrCoO$_3$. These were used to determine the anisotropic $g$-factors and van Vleck susceptibilities. The resulting temperature dependences of the susceptibility match very well the experimental data obtained on polycrystals. The calculated crystal-field split rare-earth levels for NdGaO$_3$ and PrGaO$_3$ agree well with those obtained in earlier inelastic neutron scattering experiments [9, 10]. Our results thus show that the R$^{3+}$ crystal-field parameters in oxides can be calculated with an accuracy which allows reliable prediction of the rare-earth magnetism. This knowledge may serve as a basis for interpretation of experiments in which the rare-earth ions serve as local probes of the magnetism in cobaltites [23] as well as other materials.

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Appendix A. The orthoperovskite structure

The crystal structure of RMO$_3$ perovskites (R = Pr, Nd, M = Ga, Co) consists of a pseudocubic array of the corner-shared MO$_6$ octahedra with the rare-earth cations in the cavities (see figure A.1). The orthoperovskite structure is characterized by a tilt of the octahedra by which the system responds to a size mismatch between the M and R cations. The regular twelve-fold oxygen coordination of the R site known

| Table A.1. The crystallographic data summary for RMO$_3$ compounds. Atom coordinates: Pr, Nd 4c(x, y, 1/4), Co, Ga 4b(1/2, 0, 0), O1 4c(x, y, 1/4), O2 8d(x, y, z). |
|---|---|---|---|---|
| | NdGaO$_3$ | NdCoO$_3$ | PrGaO$_3$ | PrCoO$_3$ |
| a (Å) | 5.4276 | 5.3438 | 5.4557 | 5.3737 |
| b (Å) | 5.4979 | 5.3345 | 5.4901 | 5.3395 |
| c (Å) | 7.0708 | 7.5478 | 7.7275 | 7.5729 |
| x, Pr, Nd | 0.9909 | 0.9924 | 0.9926 | 0.9957 |
| y, Pr, Nd | 0.0414 | 0.0352 | 0.0352 | 0.0290 |
| x, O1 | 0.0800 | 0.0687 | 0.0758 | 0.0669 |
| y, O1 | 0.4826 | 0.4836 | 0.4848 | 0.4946 |
| x, O2 | 0.7107 | 0.7077 | 0.7132 | 0.7178 |
| y, O2 | 0.2903 | 0.2932 | 0.2871 | 0.2827 |
| z, O2 | 0.0422 | 0.0293 | 0.0404 | 0.0357 |
for the cubic perovskites is distorted in such a way that nine R–O distances decrease and can be considered as bonding, while the four longest R–O distances gradually increase and are thus non-bonding. The resulting structure possesses an orthorhombic $Pbnm$ symmetry which is described by a four-times enlarged unit cell as shown by the crystallographic data summary in table A.1.

Table C.1. Nonzero independent parameters of the crystal field in four compounds studied. All CFPs are in units of meV.

| $k$ | $q$ | NdGaO$_3$ | NdCoO$_3$ | PrGaO$_3$ | PrCoO$_3$ |
|-----|-----|-----------|-----------|-----------|-----------|
| 2   | 0   | 28.27     | 23.76     | 30.19     | 30.19     |
| 2   | 2   | 18.75     | 6.47      | 64.44     | 64.44     |
| 4   | 0   | −52.61    | −60.52    | −57.19    | −85.52    |
| 4   | 2   | −20.63 + 83.55i | −18.52 + 85.55i | −15.88 + 95.57i | −44.12 − 48.34i |
| 4   | 4   | 20.76 − 75.35i | 23.71 − 63.86i | 44.12 − 48.34i | 44.12 − 48.34i |
| 6   | 0   | −74.44    | 121.36    | −80.84    | −104.69   |
| 6   | 2   | 11.97 + 34.56i | 10.11 + 36.99i | 9.02 + 47.49i | 9.02 + 47.49i |
| 6   | 4   | −164.72 + 0.52i | −175.20 + 0.33i | −216.61 − 1.57i | −216.61 − 1.57i |
| 6   | 6   | 15.46 − 1.95i | 11.63 + 0.48i | 15.48 − 1.51i | 16.52 − 2.33i |

Table C.2. Nd$^{3+}$ ion in NdCoO$_3$. Energy of five Kramers doublets originating from $4I_{3/2}$ multiplet, $\hat{g}$ and $\hat{\chi}^{VV}$ tensor components along the orthorhombic axes and $\omega$ direction. Energy $\varepsilon(0)$ is in meV, $\hat{\chi}^{VV}$ is in units of $\mu_B T^{-1}$.

| Doublet | $\varepsilon(0)$ | $\chi_{aa}$ | $\chi_{bb}$ | $\chi_{cc}$ | $\chi_{00}$ | $\chi_{\omega\omega}$ |
|---------|------------------|-------------|-------------|-------------|-------------|------------------|
| 1       | 0.00             | 1.701       | 2.560       | 3.015       | 1.442       | 0.0149           |
| 2       | 13.19            | 1.773       | 2.208       | 2.432       | 0.813       | −0.0072          |
| 3       | 25.66            | 3.596       | 2.524       | 1.666       | 3.800       | 0.0026           |
| 4       | 64.37            | 2.964       | 3.950       | 1.659       | 4.372       | −0.0012          |
| 5       | 84.60            | 2.576       | 2.152       | 3.009       | 1.605       | −0.0008          |

Appendix B. Effective $g$-factor

We provide a brief derivation of equation (4). For a detailed discussion of the connection between the effective $g$-factor for Kramers doublets with the $g$-factor connecting the magnetic and angular momenta the reader is referred to [19]. We start from the Zeeman Hamiltonian for the Kramers doublet

$$\hat{H}_Z = -\sum_\alpha \hat{n}^\alpha B_\alpha, \quad (B.1)$$

where $\hat{n}^\alpha$ are the Cartesian components of the magnetic moment operator. The eigenvalues of this $2 \times 2$ matrix are

$$\varepsilon_{\pm} = \pm \sqrt{\sum_{\alpha\beta} \left( m_{21}^\alpha m_{12}^\beta - m_{11}^\alpha m_{22}^\beta \right) B_\alpha B_\beta}, \quad (B.2)$$

with $m_{ij}^\alpha$ being the matrix elements of operator $\hat{n}^\alpha$ between the states of the Kramers doublet. We have used the fact that $m_{ij}^\alpha + m_{ij}^{\alpha*} = 0$ for each $\alpha = x, y, z$ due to the time reversal symmetry between the states of the Kramers doublet. Comparison with equation (3) gives the $g$-factor in the direction $(\partial_x, \partial_y, \partial_z)$ as

$$g = 2 \sum_{\alpha\beta} G_{\alpha\beta} \partial_\alpha \partial_\beta, \quad (B.3)$$

where $\sum_{\alpha\beta} G_{\alpha\beta} \partial_\alpha \partial_\beta$ is a real positive semi-definite quadratic form in the directional cosines. The eigenvalues of $G_{\alpha\beta}$ are denoted $g_x^2, g_y^2,$ and $g_z^2$.

Appendix C. The values of parameters of the crystal field and magnetic tensors

The crystal-field parameters obtained for the studied gallates and cobaltites are summarized in table C.1. They hold for...
the R position close to (0, 0, 1/4) (see table A.1) and for its inversion related counterpart close to (0, 0, 3/4), and refer to the orthorhombic coordinate system of the Pbnm structure.

The energy and the components of the $\hat{g}$ and $\hat{\chi}^{V}$ tensors of five Kramers doublets of the Nd$^{3+}$ ion in NdGaO$_3$ were summarized in table 1. Analogous data for NdCoO$_3$ are given in table C.2. The energy and the components of the $\hat{\chi}^{V}$ tensor of the nine orbital singlets of the Pr$^{3+}$ ion in PrGaO$_3$ and PrCoO$_3$ are given in table C.3.

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Table C.3. Pr$^{3+}$ ion in PrGaO$_3$ and PrCoO$_3$. Energy of nine singlets originating from $^3H_4$ multiplet, $\hat{\chi}^{V}$ tensor components along the orthorhombic axes and $\omega$ direction. Energy $\epsilon$ (0) is in meV, $\hat{\chi}^{V}$ is in units of $\mu_B$ T$^{-1}$.

| Singlet | $\epsilon$ (0) | $\chi_{\omega}$ | $\chi_{aa}$ | $\chi_{bb}$ | $\chi_{cc}$ | $\chi_{sv}$ | $\chi_{sv}$ | $\chi_{sv}$ | $\chi_{sv}$ |
|---------|---------------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1       | 0.00          | 0.0862         | 0.0991      | 0.0156      | 0.0062      | 0.00        | 0.0455      | 0.0324      | 0.0220      | 0.0107      |
| 2       | 4.45          | −0.0804        | −0.0814     | 0.0233      | 0.0063      | 8.41        | −0.0184     | 0.0343      | 0.0706      | 0.0083      |
| 3       | 14.49         | 0.3206         | 0.0173      | 0.0316      | 0.2555      | 10.94       | 0.4076      | −0.0473     | 0.0074      | 0.2444      |
| 4       | 16.04         | −0.2543        | 0.0180      | −0.0177     | −0.2545     | 12.32       | −0.4046     | 0.0243      | −0.0653     | −0.2488     |
| 5       | 21.42         | −0.0591        | −0.0366     | −0.0355     | 0.0003      | 21.15       | −0.0188     | −0.0233     | −0.0172     | 0.0009      |
| 6       | 41.03         | 0.0111         | 0.0033      | 0.0095      | 0.0234      | 42.51       | 0.0147      | −0.0008     | 0.0106      | 0.0232      |
| 7       | 54.98         | −0.0185        | −0.0011     | 0.0050      | −0.0225     | 54.43       | −0.0183     | 0.0045      | 0.0007      | −0.0179     |
| 8       | 67.04         | 0.0082         | 0.0071      | −0.0138     | 0.0197      | 65.49       | 0.0033      | −0.0069     | −0.0145     | 0.0019      |
| 9       | 89.35         | −0.0118        | −0.0234     | −0.0157     | −0.0324     | 98.78       | −0.0086     | −0.0147     | −0.0117     | −0.0201     |