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Simulation of the paramagnetic susceptibility in rare earth oxychlorides

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Abstract

The average magnetic susceptibilities of polycrystalline rare earth oxychlorides (REOCl; RE=Ce, Pr, Nd, Sm, Tb, Dy and Ho) were measured between 2 and 300 K. The susceptibility of most REOCl samples follows the paramagnetic Curie–Weiss behaviour down to low temperatures (<20 K). However, TbOCl, SmOCl, and DyOCl show additional antiferromagnetic ordering at 4, 8, and 11 K, respectively. The experimental paramagnetic susceptibilities were simulated with the aid of the van Vleck formalism based on the wave functions and energy level values obtained from a previous phenomenological simulations of spectroscopic data. The deviation of the magnetic susceptibilities of several REOCl from the Curie–Weiss behaviour at low temperatures can be explained by the gradual population of the crystal field (c.f.) components of the ground $^{2S+1}L_J$ level. At high temperatures the difference between the calculated and experimental data is due to the modification of the c.f. effect as a result of the lattice expansion. The strong preferred orientation of the REOCl crystallites may affect the experimental data because of the strong anisotropy of the paramagnetic susceptibility.

Keywords: Paramagnetic susceptibility; Rare earth oxychlorides

1. Introduction

The optical absorption and luminescence spectra of the RE^{3+} (Pr^{3+} ($4f^2$) [1], Nd^{3+} ($4f^3$) [2], Sm^{3+} ($4f^5$) [3], Eu^{3+} ($4f^6$) [4], Tb^{3+} ($4f^8$) [5], Dy^{3+} ($4f^9$) [6], Ho^{3+} ($4f^{10}$) [7], Er^{3+} ($4f^{11}$) [8], and Tm^{3+} ($4f^{12}$ electron configuration) [9]) doped RE oxychlorides have previously been studied in detail. The experimental energy level schemes were simulated with a phenomenological model taking into account simultaneously both the free ion and crystal field (c.f.) effects. Also, non-truncated sets of basis functions were used. The good agreement between the calculated and experimental energy level schemes yielded accurate wave functions associated with each level which enables the calculation of other physical properties of the RE^{3+} ions, such as the temperature dependence of the paramagnetic susceptibility [10].

In addition to the strong interactions, for example the ferro-, ferri-, or antiferromagnetic couplings between the magnetic ions, the experimental magnetic susceptibility of the RE^{3+} ions frequently deviates at low temperatures from the simple Curie(–Weiss) behaviour [10]. The aim of this report is to show how this low temperature behaviour can be analysed and explained by modelling the experimental susceptibility data with the data derived from accurate spectroscopic measurements. Accordingly, the magnetic susceptibility of the Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Tb^{3+}, Dy^{3+}, and Ho^{3+} ions in REOCl hosts were measured between 2 K and room temperature and compared with the calculated values based on the wave functions and energy level values obtained from the phenomenological simulation of spectroscopic data.

2. Experimental

2.1. Sample preparation

Since the heavier RE oxychlorides beyond ErOCl (pure ErOCl being dimorphic) possess a hexagonal structure different from the normal tetragonal one [11] the present

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study had to be restricted to the lighter oxychlorides only. The polycrystalline rare earth oxychlorides REOCl (RE= Ce–Nd, Sm, and Tb–Ho) were prepared with a solid state reaction between the corresponding RE oxides and ammonium chloride [12]. The preparation was carried out in a static N_2 atmosphere in order to avoid the reaction back to oxides. An NH_4Cl/RE oxide ratio equal to 2.15 was utilised while heating the reactants at temperatures from 900 to 1050°C for 1.5 h with decreasing temperature towards the heavier rare earths. The purity and structure of the samples was routinely verified with X-ray powder diffraction analyses and no anomalies were observed.

2.2. Paramagnetic susceptibility

The magnetic susceptibility measurements between 2 and 300 K were carried out on samples weighing ca. 10 mg with a Quantum Design MPMS-XL SQUID magnetometer applying a magnetic field of 1000 Oe. The susceptibilities were found to be independent of the magnetic field in the whole temperature range used. The experimental susceptibility values were corrected against the diamagnetic contribution by using standard values for the RE^{3+}, O^{2-}, and Cl^{-} ions [13].

For the RE compounds the difference between the experimental paramagnetic susceptibility and that predicted by the Curie–Weiss law, $\chi = C/(T-\theta)$, at low temperatures is generally due to the c.f. effect. The inadequacy of the Curie–Weiss law can be accounted for by using the formalism presented by van Vleck [14]:

$$\chi = N_A \beta^2 \sum_i \left(\frac{\langle \Phi_i | \mu | \Phi_i \rangle^2}{kT} - 2 \sum_{j \neq i} \frac{\langle \Phi_i | \mu | \Phi_j \rangle \langle \Phi_j | \mu | \Phi_i \rangle}{E_i - E_j} \right) B_i \tag{1}$$

where

$$B_i = \frac{\exp(-E_i/kT)}{\sum_i d_i \exp(-E_i/kT)} \tag{2}$$

In these expressions B_i is the thermal population coefficient for the energy levels according to the Boltzmann partition law and N_A, β, Φ, and E are the Avogadro constant, the Bohr magneton, and the non-perturbed wave functions as well as the energies of the levels in the absence of a magnetic field, respectively. The wave functions and energies were determined from the treatment of spectroscopic data. The degeneracy of the energy levels is accounted for by the term d_i.

Except for the Eu^{3+} ion possessing the non-magnetic $^7F_0$ ground level, the first diagonal part in Eq. (1), corresponding to the Curie–Weiss law, has the most important contribution to the paramagnetic susceptibility. The second, non-diagonal part is a result of the second-order perturbation and is usually of low importance, with the exception of ground states with $J = 0$.

The magnetic moment tensor operator is $\mu = (L + g_e S)$. The different values of the tensor components cause the magnetic anisotropy which, however, is observed only for an ion in a site of symmetry lower than cubic. The anisotropic components of the paramagnetic susceptibility are denoted as $\chi_\perp$ (±1 component) and $\chi_\parallel$ (0 component). For powder samples, as was the case with the RE oxychlorides, only the mean paramagnetic susceptibility $\langle \chi \rangle$ $(= [2\chi_\perp + \chi_\parallel]/3)$ can be obtained from measurements.

The wave functions Φ_i used to calculate the paramagnetic susceptibilities were provided by the simulation of the energy level schemes of the RE^{3+} ions in the REOCl hosts. The simulations were carried out by considering simultaneously both the free ion and c.f. interactions using parametrization schemes where each interaction was described by one or more parameters [15]. The free ion interactions included the electrostatic electron repulsion (the Racah parameters E_k; $k = 1$, 2, 3, or Slater integrals F^k; $k = 2$, 4, 6) and the spin–orbit coupling (the coupling constant ζ_{4f}) terms:

$$H = \sum_{k=0}^{3} E_k(nf,nf)e^k + \zeta_{4f} A_{SO} \tag{3}$$

The two- and three-body configuration interactions were included with the aid of the Trees (α, β, and γ) and Judd T^k ($k = 2$, 3, 4, 6, 7, and 8) parameters, respectively [16,17]:

$$H_{CI} = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k=2,3,4,6,7,8} T^k t_k \tag{4}$$

The spin–spin and spin–other-orbit interactions of minor importance were neglected since their effect is the greatest for the higher excited 4f levels which should have no significant, direct or indirect, contribution to the paramagnetic susceptibility. Since the effect of the higher levels on the wave functions of the lower levels cannot completely be ruled out [10], the non-truncated $4f^N$ configurations were used in all calculations in contrast to most earlier studies which have employed more or less extensive truncation schemes. The free ion parameter sets obtained (Table 1) are mutually consistent and thus provide reliable wave functions for the calculation of the paramagnetic susceptibilities. Moreover, in order to avoid any inappropriate truncation in the calculation of the paramagnetic susceptibility, the levels considered were extended up to 5000 and 10 000 cm^{-1} in energy for the diagonal and non-diagonal terms, respectively, which is largely sufficient for the temperature range studied.

The c.f. effect accounted for in the simulations followed only the standard one-electron concept since there has been no indication that the inclusion of the two-electron part improves the simulation of the lower levels. Following Wybourne's [16] formalism, the c.f. Hamiltonian was

Table 1
The free ion parameters (cm^{-1}) and selected details of the energy level simulations for the RE^{3+} ions in REOCl

REOCl	F^2	F^4	F^6	α	β	γ	ζ_{4f}	σ (cm^{-1})	No. of levels
PrOCl	67 659	49 458	32 813	23.6	−676	1422	742	17	68/91
NdOCl	70 488	50 945	35 068	19.6	−647	1791	870	20	105/182
SmOCl	78 167	55 878	39 779	19.56	−590	1654	1150	25	154/2002
TbOCl	89 471	63 055	44 081	19.58	−769	1823	1686	25	152/3003
DyOCl	91 990	64 704	46 170	19.2	−750	1860	1900	21	179/2002
HoOCl	95 105	67 548	47 518	18.94	−665	1907	2129	20	181/1001

expressed as a sum of products between the spherical harmonics C^k_q and the c.f. parameters B^k_q:

$$H_{\mathrm{c.f.}} = \sum_k \sum_{q=-k}^{q=k} \{B^k_q[C^k_q + (-1)^q C^k_{-q}] + iS^k_q[C^k_q - (-1)^{-q} C^k_{-q}]\} \tag{5}$$

The number of B^k_q parameters equals five for the C_{4v} symmetry of the RE^{3+} site in tetragonal REOCl (Table 2).

3. Results and discussion

Most of the REOCl samples studied present rather simple paramagnetic behaviour even down to very low temperatures (<20 K). However, only CeOCl almost follows the Curie law $\chi = C/T$ ($C = 0.098$ emu K mol^{-1}) in the whole temperature range studied between 2 and 300 K (Fig. 1). Practically always the temperature behaviour follows the normal Curie–Weiss law, $\chi = C/(T - \theta)$, as is the case with PrOCl, NdOCl, TbOCl, DyOCl, and HoOCl down to 10, 17, 4, 11, and 4 K, respectively (Figs. 2–6). For PrOCl and TbOCl, the Curie constants C are 1.39 and −19.36 emu K mol^{-1} and the correction terms θ are −18.80 and −11.21 K in the temperature range of 10 to 200 and 4 to 200 K, respectively. The Curie constant and correction term values for NdOCl, DyOCl, and HoOCl are as follows: 1.73, 14.14 and 13.50 emu K mol^{-1} and −58.47, −17.94 and −9.62 K, respectively. With the exception of NdOCl the deviation from the Curie–Weiss behaviour is only slight and might well be due to the c.f. effect if the ordering of the paramagnetic moments was not disturbing this evolution at even lower temperatures than 20 K.

As a striking exception, SmOCl follows the Curie–Weiss law only to a rather high temperature (ca. 85 K) (Fig. 7). The anomalous behaviour for SmOCl is probably due to the strong c.f. mixing of the c.f. components of the first excited free ion $^6\mathrm{H}_{7/2}$ level with the $^6\mathrm{H}_{5/2}$ ground level [18]. Due to the low susceptibility value this c.f. effect can be seen at an unexpectedly high deviation from the Curie–Weiss law. In contrast to SmOCl, observation of the low temperature c.f. effect is hidden for several RE oxychlorides by the antiferromagnetic ordering which occurs for TbOCl, SmOCl, and DyOCl at 4, 8, and 11 K, respectively.

The interpretation of the experimental paramagnetic susceptibilities as a function of temperature by calculations using the van Vleck formalism has earlier been proved to be feasible for several RE^{3+} ions [19,20], although some difficulties are evident as will been shown later. For the REOCl system the agreement between the calculated and experimental $1/\chi = f(T)$ curves can be considered satisfactory, at least at low temperatures. This is not abnormal since the optical measurements on which the determination of the wave functions and energy level values were based were carried out at ca. 10 K. At higher temperatures, the deviation between the experimental and calculated paramagnetic susceptibilities increases due to the increasing expansion of the crystal lattice which subsequently modifies the c.f. effect to a non-negligible extent. This behaviour could be observed for all measurements carried out for the RE oxychlorides.

In addition to this obvious high temperature c.f. effect some unexpected behaviour of the paramagnetic susceptibility was encountered. The $\chi^{-1} = f(T)$ curves for SmOCl differ considerably from each other, although the form of the curves is the same (Fig. 7). A quite similar shift was also found for SmOF [21] which could not be

Table 2
Phenomenological B^k_q parameters (cm^{-1}) for the RE^{3+} ions in REOCl. The values in parentheses refer to the estimated standard deviations

REOCl	B^2_0	B^4_0	B^4_4	B^6_0	B^6_4
CeOCl[a]	−796	−425	±788	1143	±249
PrOCl	−842(9)	−550(24)	±826(16)	1092(37)	±27(27)
NdOCl	−920(19)	−333(54)	±819(36)	934(47)	±209(45)
SmOCl	−871(15)	−527(38)	±766(26)	1006(39)	±346(41)
TbOCl	−970(16)	−591(29)	±876(16)	983(33)	±182(34)
DyOCl	−984(15)	−711(32)	±988(21)	657(33)	±158(35)
HoOCl	−1155(12)	−732(28)	±827(18)	443(24)	±58(27)

[a] The B^k_q (and $\zeta_{4f} = 638$ cm^{-1}) values for CeOCl were obtained with extrapolation using the corresponding values of the other REOCl.

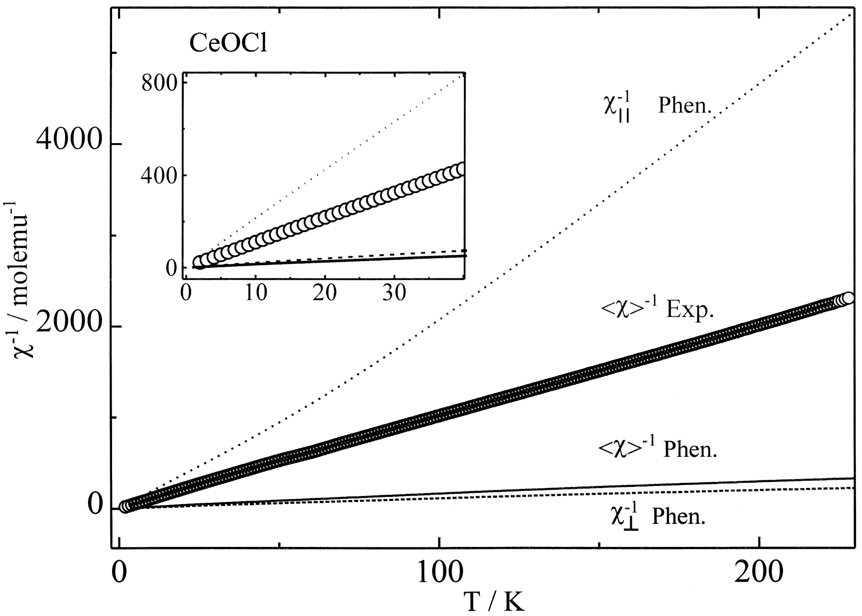

Fig. 1. Temperature evolution of the magnetic susceptibility of CeOCl.

explained at that time. An obvious reason for this discrepancy is the method of preparation of both the SmOCl and SmOF samples: the reaction between samarium oxide and ammonium halide creates a strongly reducing atmosphere, enough to reduce Pr^{4+} and Tb^{4+} in Pr_6O_{11} and Tb_4O_7, respectively (!), which decreases the amount of Sm^{3+} ($4f^5$ electron configuration) in the sample measured. The ground level ($^7F_0$) of the Sm^{2+} ion ($4f^6$ electron configuration) which is non-magnetic and subsequently results in a decrease in the total magnetic susceptibility of the sample. However, further verification of this experimental detail is under way.

The layered structure [22] and the high strength of the c.f. effect in RE oxychlorides [23] together lead to the high anisotropy in the paramagnetic susceptibility, as has been shown earlier in a study on a NdOCl single crystal [2]. Although only powder samples were available for the RE oxychlorides in this study, an indication of a similar strong anisotropy was, though only indirectly, observed for CeOCl (Fig. 1).

As revealed by the X-ray powder diffraction study of the crystal structure for the complete tetragonal RE oxychloride series (LaOCl–NdOCl, SmOCl–HoOCl, and YOCl), the crystallites of especially the heavier REOCl

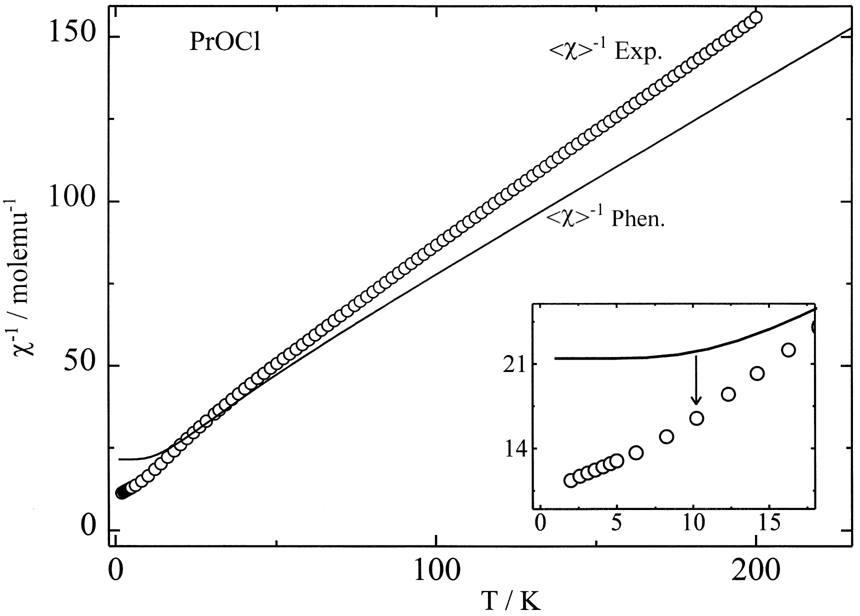

Fig. 2. Temperature evolution of the magnetic susceptibility of PrOCl.

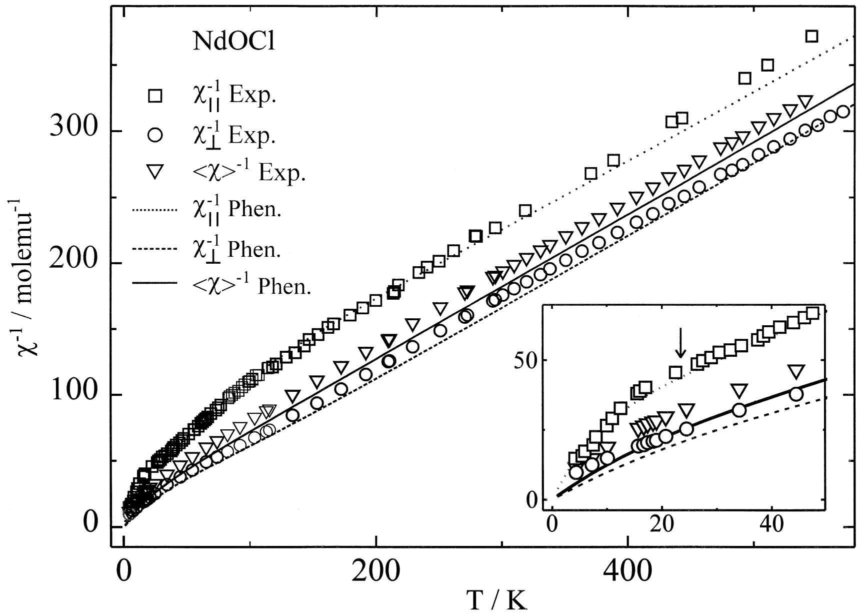

Fig. 3. Temperature evolution of the magnetic susceptibility of NdOCl. Data taken from Ref. [2] with permission of the author.

showed a strong preferred orientation perpendicular to the *c*-axis [24]. The deviation between the experimental and calculated average susceptibility values for CeOCl may be due to the non-random packing of the sample due to the preferred orientation. Even a rather slight preferred orientation in the sample packing can cause important effects since the absolute χ value is low for CeOCl. On the other hand, if some Ce^{3+} had oxidized to Ce^{4+} a similar decrease would result in the experimental susceptibility values. No low temperature c.f. effect was observed for CeOCl, in good agreement with calculations.

4. Conclusions

The experimental temperature evolution of the paramagnetic susceptibility of the RE^{3+} ion in REOCl was successfully reproduced by calculations based on the wave functions obtained from the phenomenological simulation of the energy level schemes of the corresponding $4f^N$ electron configurations. The deviation of the paramagnetic susceptibility from the Curie–Weiss law at low temperatures was explained to result from the c.f. effect. Unfortunately, the observation of this effect below 20 K was

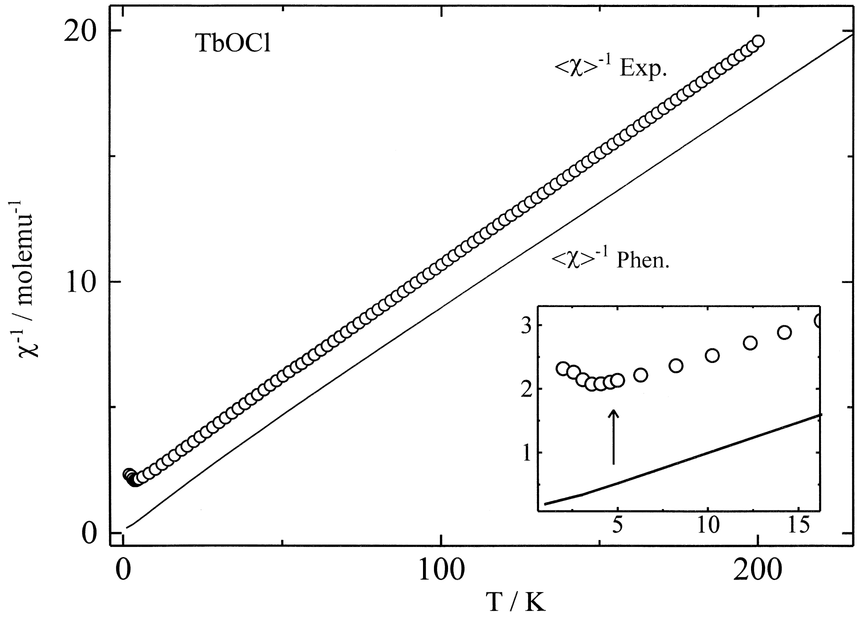

Fig. 4. Temperature evolution of the magnetic susceptibility of TbOCl.

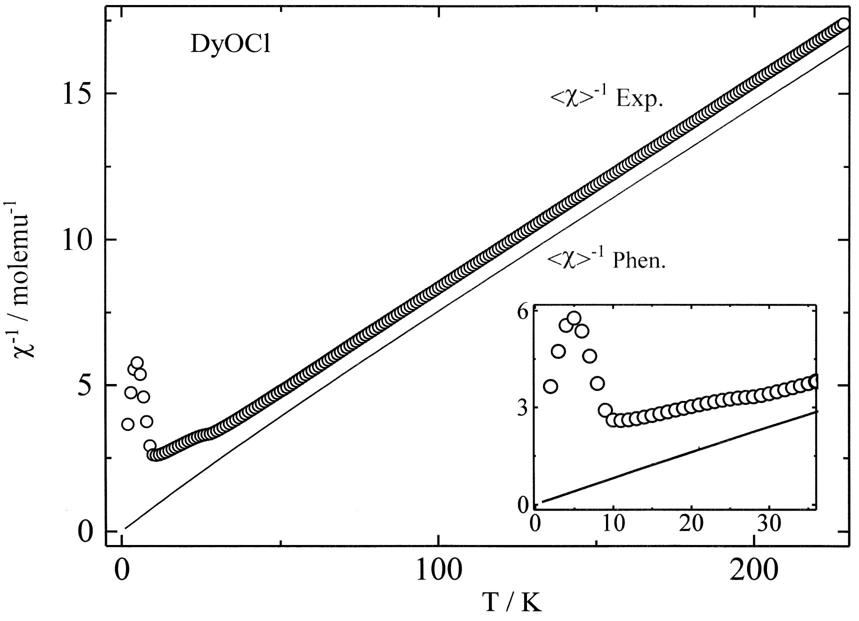

Fig. 5. Temperature evolution of the magnetic susceptibility of DyOCl.

hidden for several RE^{3+} ions by the antiferromagnetic ordering. The high anisotropy of the paramagnetic susceptibility revealed by the calculations and observed earlier for NdOCl could be indirectly observed for CeOCl where the preferred orientation of the crystallites may cause a significant difference between the calculated and experimental paramagnetic susceptibility curves. At high temperatures, lattice expansion caused discrepancies between the calculated and experimental paramagnetic susceptibilities due to the modified c.f. effect.

Despite the success in the simulation of the temperature dependence of the paramagnetic susceptibilities, some, mainly experimental, problems were encountered: for SmOCl the possible reduction of Sm^{3+} to Sm^{2+} with the non-magnetic $^7F_0$ ground level caused a decrease in the experimental paramagnetic susceptibility. However, the shapes of both curves were similar. The possible oxidation of Ce^{3+} to Ce^{4+} may cause a similar decrease in the experimental paramagnetic susceptibility for CeOCl.

Finally, one of the reasons for the differences between experimental and calculated paramagnetic susceptibilities can be due to the inclusion of the higher energy levels in

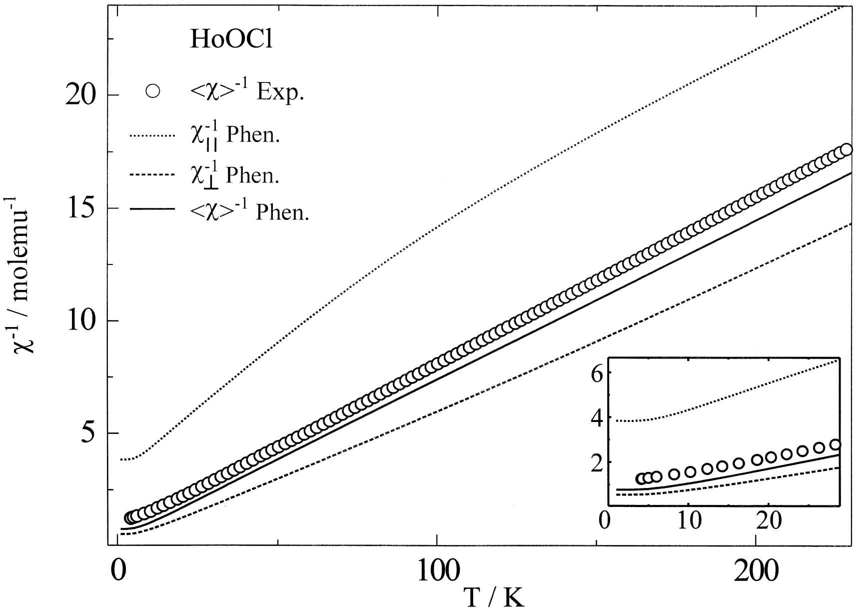

Fig. 6. Temperature evolution of the magnetic susceptibility of HoOCl.

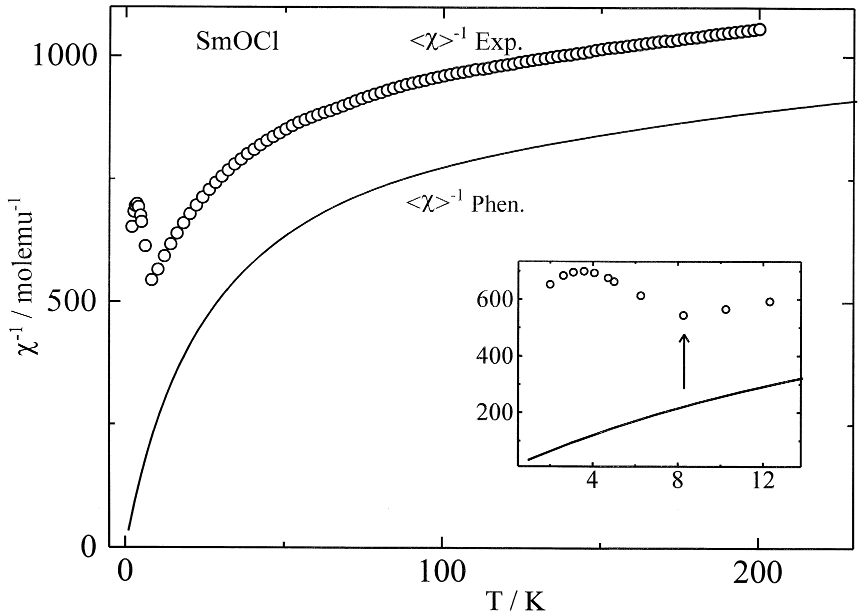

Fig. 7. Temperature evolution of the magnetic susceptibility of SmOCl.

the simulation of the spectroscopic data. Since the effect of the configuration interaction terms is still inadequately known (and thus not sufficiently taken into account), simulation of the high energy level structure distorts the energies and wave functions of the lower levels which determine the paramagnetic susceptibility. This detail has not yet been exploited but should receive much more attention.

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