Journal of Alloys and Compounds 275–277 (1998) 646–650

Correlation between the structure and paramagnetic susceptibility of NdOF

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Abstract

The high-resolution X-ray powder diffraction patterns on the polycrystalline NdOF were measured at selected temperatures between 6 and 295 K. The hexagonal unit cell constants *a* and *c* first decrease as a function of temperature as anticipated down to ca. 50 K but then suddenly a increases and *c* decreases strongly. The cell volume remains constant, however. The compression of the lattice in the direction parallel to the c-axis is due to the high anisotropy of the NdOF lattice. The rigid NdO^+ complex cation prevents the compression in the plane perpendicular to the c-axis and results in a slight dilatation in the plane. The experimental paramagnetic susceptibility measured between 3 and 850 K shows also an anomalous behavior around 50 K indicating that the structural changes influence the magnetic properties as well. The evolution of the paramagnetic susceptibility as a function of temperature was well simulated below 50 K by wave functions and energy level values obtained from inelastic neutron scattering measurements at 2.5 K. Above 50 K the simulation fails because of structural changes. The high anisotropy of the NdOF lattice was concluded to be responsible also for the anomalous behavior of the paramagnetic susceptibility as a function of temperature. © 1998 Elsevier Science S.A.

Keywords: Neodymium oxyfluoride; X-ray powder diffraction; Paramagnetic susceptibility

1. Introduction

The spectroscopic and structural properties of Nd^{3+} doped rare earth (RE) materials are among the most studied ones [1] because of the practical application as laser hosts. Neodymium oxyfluoride, NdOF, is no exception to the popularity of the neodymium compounds in scientific research. It must be admitted, however, that the use of NdOF as a laser material is most improbable since it can be obtained in powder form only. The preparation and thermal stability [2] as well as the optical properties [3] of NdOF have been studied in detail while the structure and the magnetic properties have received much less attention.

Neutron powder diffraction studies [4] have shown that the stoichiometric NdOF possesses a hexagonal crystal structure with the SmSI-type structure (space group: $R\bar{3}m$, $Z=6$). As to the electronic energy level scheme, the inelastic neutron scattering (INS) spectra measured at 2.5 K showed that the splitting of the ground $^4I_{9/2}$ level is consistent with the C_{3v} point symmetry of the Nd^{3+} site [4]. The distortions from the cubic O_h symmetry were concluded small from both structural and spectroscopic studies.

In the present work the paramagnetic susceptibility was measured as a function of temperature between 3 and 850 K. The experimental values were compared to those obtained from calculations based on the wave functions and energy level values from the inelastic neutron scattering measurements [4]. The low temperature X-ray powder diffraction (XPD) studies carried out between 6 K and room temperature yielded the unit cell dimensions. The evolution of the structural parameters and the paramagnetic susceptibility as a function of temperature was evaluated and the possible correlations between these two properties were discussed with respect to the anomalies observed.

2. Experimental

2.1. Sample preparation

The method of preparation of RE oxyfluorides, REOF, must be chosen with extreme care in order to avoid the formation of the non-stoichiometric, tetragonal $NdO_{1-x}F_{1+2x}$ phases [5]. At the same time the completion of the reaction must be ensured, i.e. the presence of the

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PII: S0925-8388(98)00411-3

sesquioxide should be avoided, too. The solid state reaction between the RE sesquioxide and ammonium fluoride [6] fulfils the requirements of a controlled preparation of the stoichiometric hexagonal NdOF and was subsequently used in this work. The mixture of Nd_2O_3 with NH_4F using a strictly stoichiometric NH_4F/Nd_2O_3 ratio (=2.00) was heated at static N_2 atmosphere at 950°C for 1 h. The sample was checked with routine XPD analysis but showed no reflections due to impurity phases.

2.2. X-ray powder diffraction

The XPD patterns of the hexagonal NdOF were measured with a laboratory made high resolution X-ray powder diffractometer [7] between 3 and 103 degrees in 2θ. The high intensity CuKβ (λ=1.39223 Å) radiation was provided by a rotating anode tube alimented by a 18 kW Rikagu generator. The measurements were carried out at selected temperatures from 6 K up to room temperature by using a T.B.T. liquid helium cryostat. The temperature stability of the cryostat was better than 0.1 K. The unit cell dimensions of the hexagonal NdOF were obtained by standard least squares calculations by using eight Bragg reflections: 006, 102, 108, 110, 208, 122, 128 and 300 in the 2θ range between 24.6 and 75.2 degrees. The estimated standard deviations in the Bragg reflection angles were smaller than 0.002 degree in 2θ.

2.3. Paramagnetic susceptibility

The paramagnetic susceptibility of the NdOF powder sample was measured with a MANICS DSM Magnetometer/Susceptometer apparatus between 3 and 850 K by using a liquid helium cryostat and a high temperature furnace. The apparatus was of the torsion balance type. The magnetic field – perpendicular to the sample rod – was kept constant at 1.6 T with stability better than 0.1%. The magnetic susceptibility of NdOF was found independent of the magnetic field which indicates pure paramagnetic behavior of the compound. The data were routinely corrected for the magnetic susceptibility of the sample holder and the diamagnetism of the sample according to the following values: -27×10^{-6}, -11×10^{-6}, and -7×10^{-6} emu mol^{-1} for Nd^{3+}, O^{2-}, and F^-, respectively.

The paramagnetic susceptibility as a function of temperature was calculated with the van Vleck formula [8] using the wave functions and energy level values of the crystal field (c.f.) levels up to 10 000 cm^{-1}. The c.f. parameters on which the calculations were based were obtained from the simulation of the splitting of the $^4I_{9/2}$ level measured by the inelastic neutron scattering (INS) of NdOF [4]. The free-ion parameters necessary to calculate the c.f. levels of other than the $^4I_{9/2}$ ground level were taken from an investigation of the optical absorption and luminescence of NdOF [3]. The actual calculations were carried out by the program REEL [9].

3. Results and discussion

3.1. Structural changes as a function of temperature

The XPD patterns of the hexagonal NdOF as a function of temperature (Fig. 1) were practically identical except for a slight increase in the total intensity of the reflections with decreasing temperature. The intensities as well as the 2θ positions of the Bragg reflections show no abrupt changes and no additional reflections or splitting of them was observed, either. Thus any major structural changes or rearrangements or appearance of new phases can easily be ruled out. However, any modifications in the magnetic behavior are not excluded but the study of them requires neutron diffraction measurements.

The expected smooth increase in the Bragg reflection positions due to the shrinking of the lattice at lower temperatures was broken down just below 140 K (Fig. 2). For NdOF, the cell volume as well as the cell dimensions seemed to stabilize to constant values between 80 and 50 K. Below 50 K, however, the lattice showed abruptly further tendency to deform. As an indication of this deformation the hexagonal axis a started to increase and c to decrease with decreasing temperature (Fig. 3) while the cell volume remained constant. The constant cell volume resulted from the cancellation of the relative thermal dilatation coefficients parallel (α_c) and perpendicular (α_a) to the c-axis. The calculation of these coefficients between 6 and 15.2 K gave the following values: $\alpha_a=(1/a)(\Delta a/\Delta T)=-39.10^{-6}$ K^{-1} and $\alpha_c=(1/c)(\Delta c/\Delta T)=+78.10^{-6}$ K^{-1} which yields: $\alpha_v=2\alpha_a+\alpha_c=0$.

The explanation to the increase and decrease in the cell parameters a and c, respectively, is rather straightforward

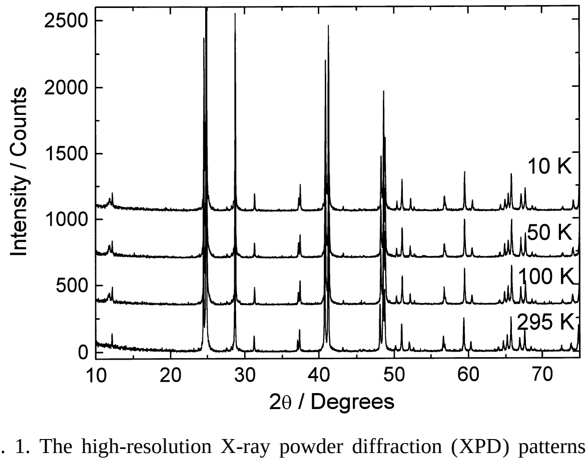

Fig. 1. The high-resolution X-ray powder diffraction (XPD) patterns of the hexagonal NdOF at 10, 50, 100 and 295 K between 10 and 75 degrees in 2θ.

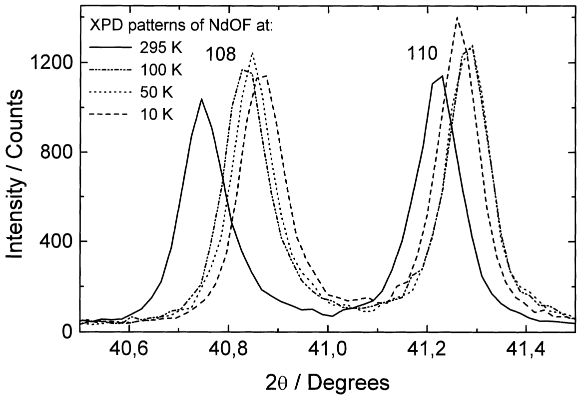

Fig. 2. Evolution of the 2θ position of the 108 and 110 Bragg reflections of the hexagonal NdOF as a function of temperature at 10, 50, 100 and 295 K.

if one keeps in mind the structural characteristics of all RE oxycompounds [10]: the overall structure – irrespective of the type being a trigonal one as the RE oxyfluorides [11] or a tetragonal one as the most other RE oxyhalides [12] – is composed of layers of the complex cation $[\mathrm{REO}]_n^{n+}$ and the anion X^{n-} perpendicular to the c-axis. The complex cation $[\mathrm{REO}]_n^{n+}$ is a very rigid structural unit possessing important covalent bonding while the bonding to the anion layer is primarily ionic and can lead in the macroscopic scale to intercalation of other anions or even organic molecules to the anion layer. The RE oxycompounds show also easy cleavage along the ab-plane. It is thus no wonder that this high anisotropy results in the easy compression of the lattice along the c-axis which is compensated by the dilatation in the a-axis direction in a way to yield constant volume.

The spectroscopic studies on the electronic absorption spectra of NdOF [3] support the conclusions from the present XPD results that no major changes in the structure is to be expected despite the anomalous behavior of the unit cell parameters. In the next chapter, it will be shown, however, that the structural deformations as a function of temperature can indeed lead to changes in the magnetic properties of NdOF.

3.2. Paramagnetic susceptibility as a function of temperature

The experimental paramagnetic susceptibility as function of the temperature (Fig. 4) shows that NdOF is paramagnetic down to 3 K. No orientation of the individual magnetic moments leading to ferro- or antiferromagnetic behaviour could be observed. The reciprocal susceptibility curve as a function of temperature decreases by no means monotonously: three domains can be distinguished between 3 and 295 K. This behaviour will be discussed later. For the two regions below and above the 55 K which fulfil the Curie–Weiss law $\chi = C/(T+\theta)$, slightly different values for the two constants were obtained: $C=1.30$ and 1.36 K; $\theta=17.3$ and 24.4 K, respectively. The two regions may well be due to a structural modification discussed earlier in Section 3.1.

The Nd^{3+} ion (the 4f^3 electron configuration) is one of the best ones for theoretical considerations since the degeneracy of the configuration is still reasonable, i.e. only 182 Stark levels (Kramer's doublets) are present facilitating considerably the calculations. The low number of c.f. levels enables also the simultaneous treatment of the free ion (electronic repulsion, spin-orbit coupling and both the two and three body configuration interaction terms) and c.f. interactions. The relatively high point symmetry of the Nd^{3+} site in NdOF splits the 364×364 square matrix for the complete energy level scheme further into two submatrices of the sizes 120×120 and 124×124 [13]. The paramagnetic susceptibility of the Nd^{3+} ion at any temperature can thus be calculated using the van Vleck formula [8] with no major problems as successfully shown e.g. for NdF$_3$ [14]:

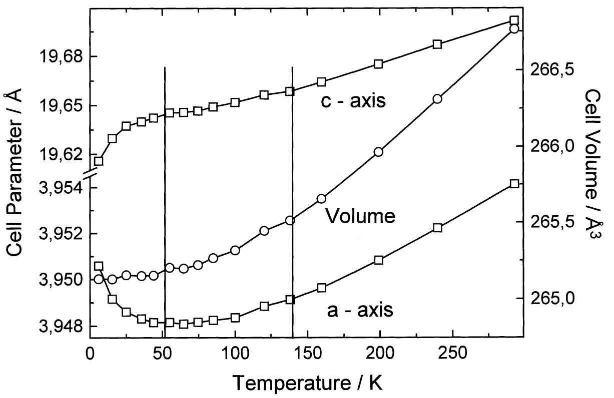

Fig. 3. Evolution of the unit cell parameters *a* and *c* as well as the cell volume of the hexagonal NdOF as a function of temperature between 6 and 295 K.

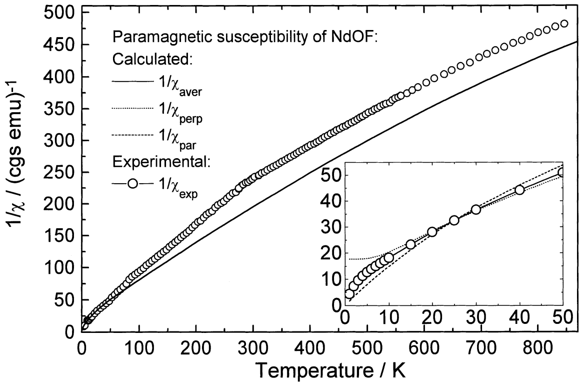

Fig. 4. The calculated (lines) and measured (points) paramagnetic susceptibility of NdOF as a function of temperature between 3 and 850 K. The inset shows the strong anisotropy of the magnetic susceptibility at low temperatures.

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

where

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

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, the non-perturbed eigenfunctions and eigenvalues of the energy levels in the absence of a magnetic field, respectively. The degeneracy of the energy levels is accounted for by the term d_i. The magnetic moment operator is $\mu = (L + g_e S)$.

Below 55 K the susceptibility follows nicely the value calculated by the van Vleck formula (Fig. 4) which clearly supports the unique and correct nature of the c.f. parameters set obtained by fitting the c.f. split $^4I_{9/2}$ ground level alone. Above 55 K but below 140 K a less good agreement is obtained between the experimental and calculated susceptibilities. At even higher temperatures ($T > 300$ K) the experimental curve follows well the calculated one but there is a constant shift between the two values. This is in agreement with the XPD results which showed irregular behaviour to occur between 50 and 140 K. Taken into account that the splitting of the $^4I_{9/2}$ ground level was measured at 2.5 K and the paramagnetic susceptibility calculations were carried out according to wave functions obtained from calculations on this data it is no wonder that an excellent agreement obtained between the experimental and calculated values occurs below 50 K only.

Although deviations of the experimental paramagnetic susceptibility from the calculated values as function of the temperature are not completely unknown as shown in [15], the reason for the deviation should be searched in two sources: either the wave functions for the lowest Stark levels of the ground ^4I term are not correct or the lattice is subject to an abnormal behaviour during the temperature change. For NdOF, the latter seems more probable in view of the similarity of the absorption spectra as a function of temperature [3].

During the simulation of the susceptibility data it became evident that the calculated average susceptibility was rather insensitive to the actual c.f. parameter values. In fact, several sets of c.f. parameters could reproduce the average susceptibility in a reasonable manner, even if the parameter values had only distant resemblance to the correct one. In contrast, the anisotropy at the low temperature range (below 30 K, see inset of Fig. 4) changed drastically along with the c.f. parameter values. This is in accordance with the structural data available. It might be that the anomalous evolution in both the unit cell parameters and the paramagnetic susceptibility are due to the strong anisotropy of the NdOF lattice.

4. Conclusions

The X-ray powder diffraction and paramagnetic susceptibility measurements carried out as a function of temperature between 3 and 300 K revealed both anomalies at low temperatures below 140 K. The anomalous behaviour in the unit cell dimensions and paramagnetic susceptibility are probably due to the strong anisotropy of the NdOF lattice with a quasi two-dimensional structure of alternating $(NdO)^+$ and F^- layers perpendicular to the c-axis. The anisotropy of the lattice was revealed also by the calculation of the paramagnetic susceptibility based on the wave functions and the level energies obtained from inelastic neutron scattering measurements at 2.5 K. Modifications in the magnetic properties, invisible from the X-ray diffraction measurements, cannot, however, be ruled out as a reason for the anomalies observed. In order to explain the anomalies observed, complementary neutron powder diffraction measurements will be carried out to cast more light to the structural details, i.e. the atomic positions of the light oxygen and fluoride elements. The possible modifications in the magnetic properties of NdOF can then be investigated as a function of temperature, as well. Finally, it became evident that the sets of c.f. parameters, i.e. the extent of the c.f. effect, deduced from the measurement and reproduction of the paramagnetic susceptibility, cannot be considered reliable since many, usually very different c.f. parameter sets, can yield similar behaviour of the average experimental susceptibility curve as a function of temperature. However, the reproduction of the anisotropy in the susceptibility requires exact wave functions and energy level values.

Acknowledgements

Financial aid from the Academy of Finland (project #4966) to the authors (J.H. and E.S.) is gratefully acknowledged. The authors are indebted to Dr. P. Porcher (U.P.R. 209, C.N.R.S., France) for the use of the matrix diagonalization program REEL which yielded the calculated magnetic susceptibility of NdOF as a function of temperature.

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