MAGNETIC PROPERTIES OF LAYERED EUOCL AND EUOBR MATERIALS: INVESTIGATIONS AND MATHEMATICAL SIMULATION

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The polycrystalline EuOCl and EuOBr samples were prepared by heating intimately ground mixtures of europium oxide, Eu_2O_3 and ammonium chloride, NH_4Cl in static N_2 atmosphere. The magnetic susceptibilities for Eu^{3+}(Eu^{2+}) ions in polycrystalline tetragonal europium oxychloride and oxybromide were measured in temperature region between 4,2 and 310 K. The susceptibilities of EuOCl and EuOBr follow the paramagnetic Curie–Weiss behavior down to low temperatures. The temperature dependence of the experimental paramagnetic susceptibility for EuOCl and EuOBr was simulated with the aid of the van Vleck formalism.

1. Introduction

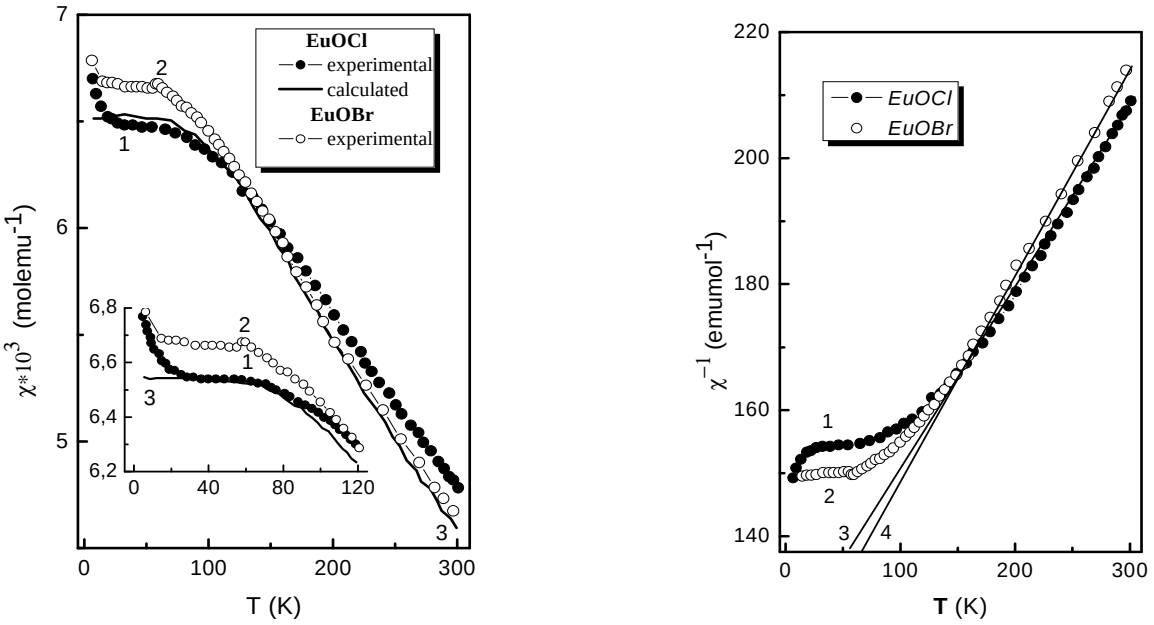
Oxyhalides of rare earth elements (LnOHal; Ln- lanthanide; Hal = F; Cl; Br; I) are very interesting materials which find various applications as X-ray luminescent screens, as anti- Stokes (frequency up shift) converters, commercial phosphors, e.g. CRT displays and photosimulated materials . Moreover, these crystals are of essential interest in connection with the research and development work on laser materials and optoelectronic devices [1-3]. The layered structure of rare earth oxycompounds suggests that materials of this type may exhibit 2D electronic and magnetic behavior. The quasi-2D nature of the host lattice has been confirmed e.g. by energy transfer and migration studies [4, 5].

Magnetic coupling between Ln^{3+} ions is usually weak resulting in a Curie–Weiss type paramagnetic behaviour down to low temperatures. It is thus difficult to infer with certainty the nature or even the temperature of the magnetic ordering. The strong anisotropy of the rare earth oxyhalide structure5 may also be reflected in the magnetic properties. The Ln^{3+} ions have low-lying multiplets with high J-values and when these are split further by the strong crystal field of uniaxial C_{4v} symmetry in LnOHal interesting magnetic phenomena might be observed [5].

2. Experimental

The polycrystalline europium oxyhalide, EuOHal, samples were prepared by heating intimately ground mixtures of europium oxide, Eu_2O_3 and ammonium halide, NH_4Hal in static N_2 atmosphere. The solid state reaction between these compounds takes place at a temperature 200^{o}C. Details of the sample preparation technique can be found elsewhere [2]. The X-ray phase analysis were performed by a X-ray diffractometer HZG4 (CuK_α–radiation) and analyzed by Rietveld method. The room temperature diffraction data indicated the samples to be of high quality since all observed reflections could be indexed using the tetragonal space group *P*4/*nmm*. The microstructure analysis was carried out by microscope Neophot 21. The DTA pattern were recorded by commercial measurement system Setaram TGDTA 92. Magnetic susceptibility measurements were carried out between 4,2 and 300 K on EuOCl and EuOBr powder samples weighing between 84 and 310 mg with a standard mutual inductance system (used Lock-in SR 530) and vibrations sample magnetometer using an applied magnetic field of 0,001-0,15 T. Only the average paramagnetic susceptibility $\chi_{ave} = (2\chi_{\square} + \chi_{\perp})/3$ could be measured for the powder samples because of the a priori random orientation of crystallites [4]. The experimental susceptibility values

were corrected for the contribution of the sample holder as well as for the diamagnetism of the sample itself by using standard values for the Eu^{3+}, O^{2-} and $Cl(Br)^{-}$ ions [5].



(a) **(b)**

Fig. 1. Temperature dependences of the magnetic susceptibility χ (**a**) and χ^{-1} (**b**) of EuOCl and EuOBr. The solid line describes the Curie–Weiss behaviour(**b**, lines 3 and 4) and the mathematical simulated paramagnetic susceptibility (**a**, curve 3).

3. Results, discussion and conclusion

For the rare earth compounds the difference between the experimental paramagnetic susceptibility and that predicted by the Curie–Weiss law, $\chi = C/(T-\theta)$ ($C = N_A\mu_{eff}^2/3k$, where C is the Curie constant, θ the Weiss constant, N_A Avogadro's number, μ_{eff} the effective magnetic moment, and k Boltzmann's constant), 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 [6]

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

$$B_i = \exp(-E_i/kT)/\sum_i d_i\exp(-E_i/kT) \quad (2)$$

in this expression, *Bi* 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 level energies in the absence of a magnetic field, respectively. μ is the magnetic dipole operator *L+geS*. The wave functions and energies were given by the treatment of the spectroscopic data [7]. The degeneracy of the energy levels is accounted for by the term d_i. The actual calculations were carried out with the original program package developed in our laboratory.

The direct and inverse of magnetic susceptibility data, χ_{ave} and $1/\chi_{ave}$, measured for the EuOCl and EuOBr powder samples as a function of temperature, are shown in Fig. 1 (a and b, respectively). Also depicted are the magnetic susceptibility data, $\chi_{ave} = f(T)$, and, in the insets, the low temperature part of the $1/\chi_{ave} = f(T)$ curve for the majority of interesting cases. The high temperature

inverse susceptibility data were fitted to the Curie–Weiss law $\chi = C/(T-\theta)$ and the resulting linear plots were superimposed on the experimental data.

EuOCl and EuOBr samples studied thus present paramagnetic behavior down to low temperatures. However, at temperatures lower than 30–100 K, significant deviation from the linear Curie–Weiss behavior was observed for nearly every $1/\chi_{ave}$ curve. This difference may be attributed either to the crystal field effect on the $4f^N$ energy level scheme or to exchange interactions in the Eu^{3+} sublattice [4, 5].

The temperature dependence of the inverse magnetic susceptibility of EuOBr (Fig. 1b) is complex: characteristic to a Curie–Weiss paramagnet at high temperatures, constant for the lower temperature range between 55 and 15 K and then sharply decreasing below 8 K. This behavior can be qualitatively explained by the exceptional ^7F_J (J = 0–6) ground term energy level scheme of the Eu^{3+} ion [2, 4]. The $^7F_0$ ground level is non-magnetic and gives no contribution to the susceptibility of EuOBr at low temperatures. Below 10 K, the sharp decrease in the inverse susceptibility is probably due to the presence of a slight amount of Eu^{2+} impurity. The Eu^{2+} ion with the $4f^7$ electron configuration has high paramagnetic susceptibility. The Eu^{2+} impurity is present because of the reduction of Eu^{3+} by decomposing NH_4Br during the preparation of EuOBr [4].

The temperature evolution of the paramagnetic susceptibility for the EuOBr was mathematical simulated in a satisfactory manner with the van Vleck model (eqns. 1 and 2) using data for the free ion.

4. References

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МАГНІТНІ ВЛАСТИВОСТІ ШАРУВАТИХ МАТЕРІАЛІВ EuOCl ТА EuOBr: ДОСЛІДЖЕННЯ ТА МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ

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Полікристалічні зразки EuOCl та EuOBr були синтезовані в процесі нагрівання суміші оксиду європію Eu_2O_3 та хлориду амонію NH_4Cl в статичній атмосфері обезводненого азоту. Магнітна сприйнятливість іонів $Eu^{3+}(Eu^{2+})$ в полікристалічному тетрагональному оксихлориді та оксибромідіі європію були виміряні в температурному інтервалі 4,2 – 310К. Температурна поведінка магнітної сприйнятливості EuOCl та EuOBr задовільно описується в рамках закону Кюрі-Вейса аж до діапазону низьких температур. Температурна залежність експериментально виміряної парамагнітної сприйнятливості EuOCl та EuOBr була змодельована в рамках формалізму Ван Флека.