

Paramagnetic properties of several rare earth compounds with $K_3Ln_2(NO_3)_9$ structure

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Received 28 June 2005; accepted 19 October 2005

Abstract

We present measurements of the paramagnetic susceptibilities of $K_3Pr_2(NO_3)_9$ and $K_3Sm_2(NO_3)_9$, cubic materials with rare earth sites having threefold rotational symmetry about (111). The rare earth environment resembles that of the $Ln_2Mg_3(NO_3)_{12} \cdot 24H_2O$ materials, and the magnetic susceptibilities show similarities but also interesting differences with $Pr_2Mg_3(NO_3)_{12} \cdot 24H_2O$ and $Sm_2Mg_3(NO_3)_{12} \cdot 24H_2O$. Paramagnetic resonance experiments in $K_3La_2(NO_3)_9$ doped with these and several heavier lanthanides are also described and compared with theory. © 2005 Elsevier Ltd. All rights reserved.

PACS: 75.20.Ck

Keywords: A. Magnetic materials; D. Magnetic properties; D. Crystal fields

1. Introduction

The anhydrous rare earth double nitrates $K_3Ln_2(NO_3)_9$ are cubic, space group O^6-P4_32 , with the Ln^{3+} ions occupying the 8 (c) sites, having a C_3 rotational symmetry axis parallel to (111) [1,2]. Fig. 1 shows the arrangement of the rare earth ions in the cubic unit cell, with magnetic nearest neighbors indicated. The rare earth environment in the $K_3Ln_2(NO_3)_9$ materials resembles that in the well-known hydrated double nitrates with the rhombohedral ($C_{3i}^2 - R\bar{3}$) structure of $Ln_2Mg_3(NO_3)_{12} \cdot 24H_2O$ or LnMN. In both structures, the rare earth ions have the same C_3 point symmetry, and are surrounded by twelve oxygen atoms belonging to six nitrate groups, located at the corners of a somewhat distorted icosahedron [3]. The average lanthanide-oxygen distance is virtually identical in the two cases: 2.63 Å in $K_3Pr_2(NO_3)_9$, 2.64 Å in CeMN. Both structures contain two structurally distinct groups of nitrate ions. Both also form only for La through Eu; the oxygen icosahedron is not stable for smaller lanthanide ions [4]. These resemblances suggest that the crystal field environment, and possibly the magnetic g tensor, might be similar in the two classes of materials, even though the lattice

symmetry is quite different. Previously known examples of this sort have typically shared the same lattice symmetry, e.g. the hexagonal rare earth ethyl sulfates and rare earth trifluoromethane sulfonates [5,6].

The LnMN-structure materials display a variety of interesting magnetic characteristics, including ionic level splittings which in some cases are predicted to surprising accuracy by an icosahedral crystal field [7–10]. Magnetic interactions in the hydrated double nitrates are primarily dipolar, with ordered magnetic ground states predicted by the dipolar interaction alone [11]. We were motivated to study the magnetic properties of the $K_3Ln_2(NO_3)_9$ materials by the close similarity to the unusual icosahedral crystal field environment in the $Ln_2Mg_3(NO_3)_{12} \cdot 24H_2O$ compounds, coupled with the novelty of a cubic lattice. In previous work we have found the g tensor of $K_3Nd_2(NO_3)_9$ is rather close to that of the corresponding $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$, but those of the Ce compounds are not similar [12,13]. The Ce and Nd compounds order antiferromagnetically, but the isostructural $Na_3Gd_2(NO_3)_9$ is a ferromagnet. In this paper, we present results for the Pr and Sm compounds of this series, which remain paramagnetic to temperatures as low as 10 mK.

2. Experimental methods

Polycrystalline $K_3Pr_2(NO_3)_9$ and $K_3Sm_2(NO_3)_9$ were grown by the molten flux technique [1,12]. Grain sizes as large as 3–4 mm were obtained, which could be broken out to provide

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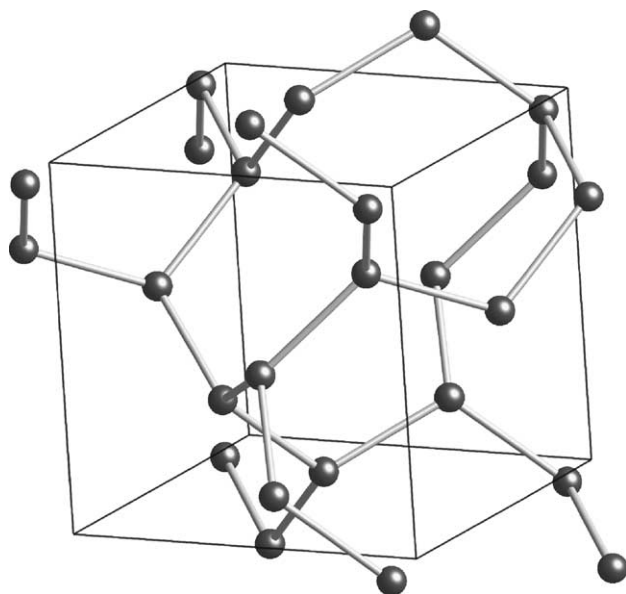


Fig. 1. The cubic unit cell of the $K_3Ln_2(NO_3)_9$ structure, showing the rare earth ions only, with links shown between nearest magnetic neighbors. Each ion has three nearest neighbors, forming a flattened tetrahedron with a threefold symmetry axis along (111).

single crystals for study. Powder X-ray diffraction spectra yielded cubic lattice constants of 13.545 and 13.479 Å for the Pr and Sm compounds, respectively, in reasonable agreement with previously reported values [1]. Static magnetic susceptibilities were measured using shaped single-crystal spherical samples with diameters of 1–2 mm, coated with vaseline to prevent water absorption from the atmosphere. Measurements above 1.7 K were made using a Quantum Design MPMS SQUID magnetometer, and below 2.5 K with fluxgate magnetometers in a dilution refrigerator, as described previously [12,13]. Paramagnetic resonance measurements were taken with a Bruker ECS 106 spectrometer at temperatures between 2 and 3 K.

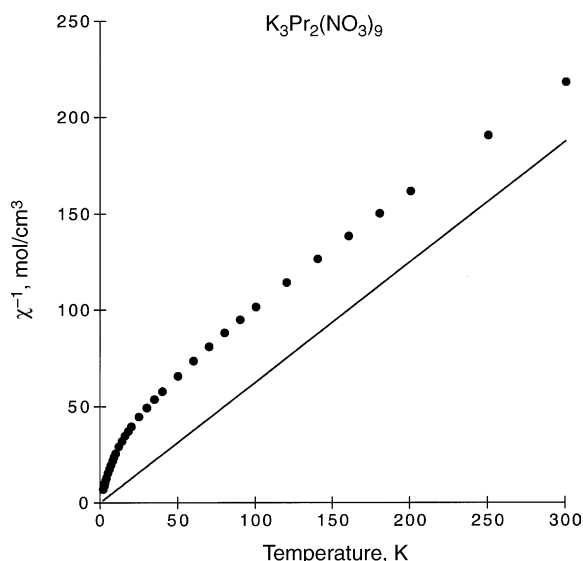


Fig. 2. Inverse susceptibility of $K_3Pr_2(NO_3)_9$ versus temperature from 2 to 300 K. The dashed line is the free ion susceptibility.

3. Results and discussion

The high- and low-temperature magnetic susceptibilities of $K_3Pr_2(NO_3)_9$ are shown in Figs. 2 and 3, respectively. The $J=4$ ground multiplet of Pr^{3+} is split by the trigonal crystal field into three singlets and three non-Kramers doublets. From perhaps 0.5–3 K a Curie–Weiss law is followed fairly well, with a Curie constant of $C=0.332\pm 0.007\text{ cm}^3\text{ K/mol}$ and $\theta=-0.38\pm 0.05\text{ K}$. Below 0.5 K the susceptibility exhibits temperature-independent paramagnetism, indicating a small splitting between a singlet ground state and the first excited state of Pr^{3+} . The data show some thermal hysteresis in this region, probably due to poor thermal equilibrium. At temperatures below $\sim 0.1\text{ K}$, a hyperfine contribution is visible in the susceptibility.

The crystal field parameters and splittings of $K_3Pr_2(NO_3)_9$, as well as the other compounds in this series, have not been independently measured. In the structurally related $Pr_2Mg_3(NO_3)_{12}\cdot 24H_2O$ (PrMN), a doublet ground state is found, which is split by about 0.18 cm^{-1} due to distortions in the crystal field [14]. If we assume that the Curie–Weiss region in $K_3Pr_2(NO_3)_9$ is likewise due to a single ground non-Kramers doublet, the (isotropic) susceptibility would imply $g_{\parallel}=3.26$, $g_{\perp}=0$. This value is slightly more than twice that found in PrMN [4,15]. We observed no resonance in a conventional EPR measurement of $K_3La_2(NO_3)_9: Pr^{3+}$, consistent with $g_{\perp}=0$. If we assume further, as suggested in PrMN, that a doublet ground state is split into ground and excited singlets $|0\rangle$ and $|1\rangle$ by distortions in the crystal field, the electronic susceptibility extrapolated to $T=0$ can be compared to $\chi_{0,\parallel}(T=0)\cong N_0(g_J\mu_B)^2(2|\langle 0|J_z|1\rangle|^2/\Delta)$, where χ_0 is the susceptibility of noninteracting ions: $(1/\chi)=(1/\chi_0)-\lambda$, in the mean field approximation, and $\lambda=\theta/C$. This formula, which assumes the splitting Δ between $|0\rangle$ and $|1\rangle$ is small compared

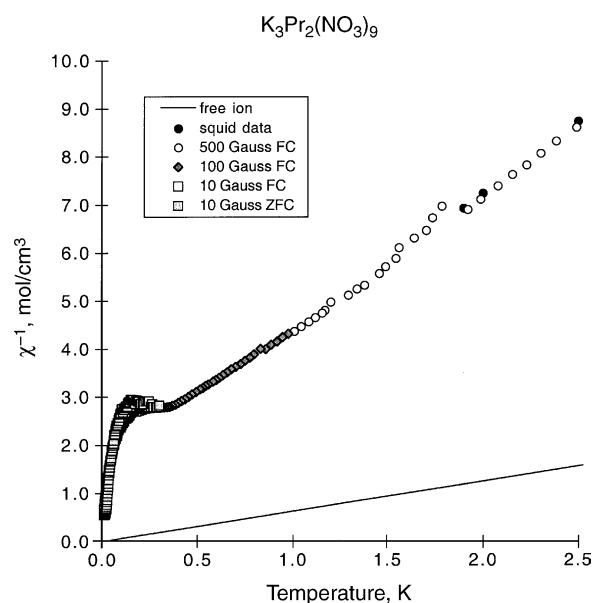


Fig. 3. Susceptibility of $K_3Pr_2(NO_3)_9$ below 2.5 K. Temperature-independent van Vleck paramagnetism is apparent below about 0.5 K, with a hyperfine contribution below 0.1 K.

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