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Magnetic Effect Studies of Rare Earth-Containing Apatites

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Magnetic susceptibility measurements of phosphate and silicate apatites of the $A_{10-2x}Ln_xM_x(PO_4)_6Y_2$ (A = Sr,Pb; Y = F, Cl; x = 1, 2) and $Sr_2Ln_8(SiO_4)_6O_2$ types with Ln = Nd and Gd showed no magnetic order of the rare earth ions down to liquid He temperature. Temperature dependence showed theoretical contributions of the Gd^{3+} ions and a negative deviation for the Nd^{3+} ions. Curie temperatures were all of positive values. Magnetic behavior of apatite-type compounds is discussed in view of their bond lengths.

Introduction

Rare earth ions, together with the alkaline earth and lead ions, are known as apatite-building cations. They were investigated in different apatite systems in connection with the use of rare earth-substituted apatites as laser materials and in order to study substitution processes in apatites of biological systems. In phosphate or arsenate apatites the divalent alkaline earth metals can be substituted only by a limited number of rare earth ions (*1, 2*), whereas in silicate apatites rare earth ions occupy most of the cationic positions of the lattice.

$M_2Ln_8(SiO_4)O_2$-type apatites crystallize in the $P6_3/m$ hexagonal structure of the apatites (*3, 4*). In this structure cations are located in two crystallographically nonequivalent positions. In a recent work (*5*) single-crystal structure analysis of $Ca_2La_8(SiO_4)_6O_2$ has revealed that the 6*h* site of the lattice is occupied solely by the lanthanum ions and the 4*f* sites equally by La^{3+} and Ca^{2+} ions.

Magnetic susceptibility studies of $Eu_5(PO_4)_6F$ and $Eu_5(PO_4)_6Cl$ above 4 K (*6*) and of $Pb_6Nd_2Na_2(PO_4)_6Cl_2$ above 2 K (*7*) have shown that rare earth ions in these compounds do not order magnetically.

TABLE I

LATTICE CONSTANTS AND EFFECTIVE MAGNETIC MOMENTS (μ_B) OF RARE EARTH-CONTAINING APATITES (TEMPERATURE RANGE 4.2–40 K)

Compound	Lattice constants		μ_B	μ_B
	a(Å)	c(Å)	obsd	calcd
$Pb_6Nd_2Na_2(PO_4)_6F_2$	9.661	7.067	2.7	3.6
$Pb_6Nd_2Na_2(PO_4)_6Cl_2$	9.772	7.199	3.2	3.6
$Sr_6Nd_2Na_2(PO_4)_6Cl_2$	9.800	7.193	2.9	3.6
$Pb_6Nd_2K_2(PO_4)_6F_2$	9.760	7.275	2.7	3.6
$Pb_6Gd_2Na_2(PO_4)_6F_2$	9.712	7.158	7.2	7.9
$Pb_8GdNa(PO_4)_6F_2$	9.771	7.252	8.3	7.9
$Sr_2Nd_8(SiO_4)_6O_2$	9.585	7.118	3.5	3.6
$Sr_2Nd_6La_2(SiO_4)_6O_2$	9.615	7.144	3.1	3.6
$Sr_2Nd_4La_4(SiO_4)_6O_2$	9.642	7.174	3.2	3.6
$Sr_2Nd_2La_6(SiO_4)_6O_2$	9.670	7.204	3.2	3.6
$Sr_2Nd_7Gd(SiO_4)_6O_2$	9.566	7.078	—	—
$Sr_2Gd_4La_4(SiO_4)_6O_2$	9.582	7.082	—	—

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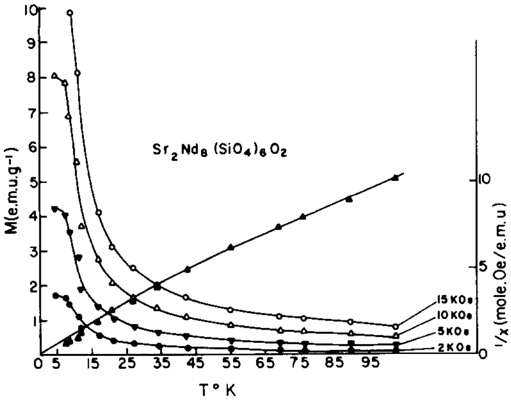

FIG. 1. Magnetization versus temperature at different applied fields and reciprocal susceptibility vs temperature for $Sr_2Nd_8(SiO_4)_6O_2$.

Experimental

The silicate compounds were prepared by a firing process in which stoichiometric amounts of $SrCO_3$, Ln_2O_3 (Ln = La, Nd, or Gd), and SiO_2 were heated in a platinum tube at about 1400°C during 2 days. After the first 24 hr heating the sample was ground and reheated for an additional 24 hr. The phosphate apatites were synthesized by a method described elsewhere (*1*, *2*). The powdered samples were X-ray analyzed by a Philips diffractometer using monochromatized Cu*K*α radiation. The purity of the samples, as well as the cell constants of the apatite phase, was determined by the X-ray diffraction patterns of the compounds.

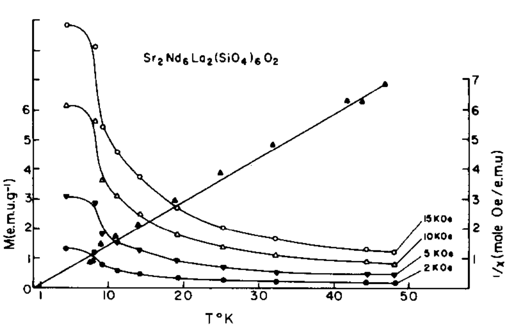

FIG. 2. Magnetization versus temperature at different applied fields and reciprocal susceptibility vs temperature for $Sr_2Nd_6La_2(SiO_4)_6O_2$.

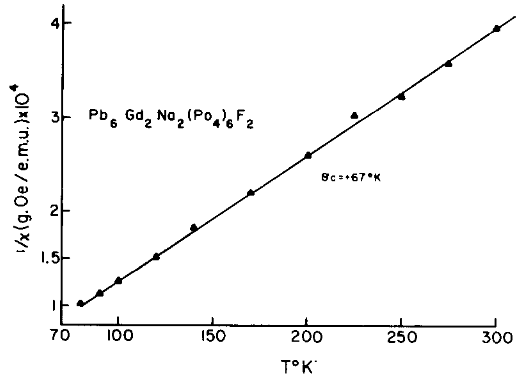

FIG. 3. Reciprocal susceptibility versus temperature for $Pb_6Gd_2Na_2(PO_4)_6F_2$.

Magnetic susceptibility measurements were carried out in the temperature range between 4.2 and 300 K in magnetic fields up to 15 kOe, using a PAR vibrating-sample magnetometer (Model 155). Estimated deviation of μ_B is $\pm 0.1\ \mu_B$.

The Mössbauer studies of the 86.5-keV γ ray of ^{155}Gd in $Sr_2Nd_7Gd(SiO_4)_6O_2$ were carried out at 4.2 K. The source used was in the form of $^{155}SmPd_3$. The experimental spectra were analyzed by least-squares computer fits.

Results

Table I lists the rare earth-containing apatites investigated in this work. From the point of view of their crystal structure, all

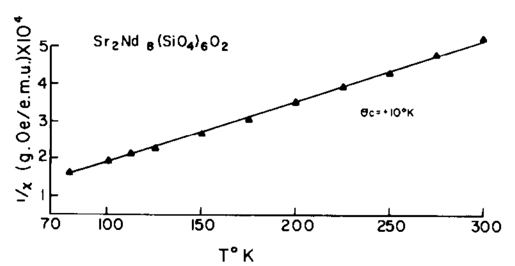

FIG. 4. Reciprocal susceptibility versus temperature for $Sr_2Nd_8(SiO_4)_6O_2$.

crystallize in the apatitelike hexagonal structure. X-Ray diffraction analysis of the samples has proved this and also that all the observed reflections belong to the hexagonal lattice, characteristic for the apatite structure. The lattice constants calculated agreed well with what is known for these compounds (*1–4*). The phosphate apatites were selected mainly from the lead–rare earth system, because in this group the composition could be varied by the addition of Na^+, K^+, F^-, and Cl^- ions. In the case of the silicate apatites the magnetic measurements included a series of solid solutions in which the paramagnetic Nd^{3+} and Gd^{3+} ions were gradually replaced by La^{3+}.

The reciprocal magnetic susceptibility values obtained in the low-temperature range (4.2–40.0 K) were plotted vs temperature and resulted in an almost straight line. Figures 1 and 2 show two such representative curves. The μ_B values calculated from these curves, together with the theoretical μ_B values, are listed in Table I. Experimental μ_B values were always lower in the Nd-containing compositions and somewhat higher in compounds with Gd. For a number of compounds the magnetic susceptibility vs temperature was also measured in the 80- to 300-K range (Figs. 3 and 4). For all the compounds measured, the change of $1/\chi$ with the temperature was linear for all temperatures. Table II shows the μ_B and Curie temperature (Θ_C K) values obtained.

TABLE II

EFFECTIVE MAGNETIC MOMENTS (μ_B) AND CURIE TEMPERATURE (Θ_C) OF RARE EARTH-CONTAINING APATITES (TEMPERATURE RANGE 80–300 K)

Compound	μ_B obsd	μ_B calcd	Θ_C (K)
$Pb_8GdNa(PO_4)_6F_2$	8.2	7.9	+35
$Pb_6Gd_2Na_2(PO_4)_6F_2$	8.1	7.9	+67
$Sr_2Gd_4La_4(SiO_4)_6O_2$	8.1	7.9	+54
$Sr_2Nd_8(SiO_4)_6O_2$	3.4	3.6	+10

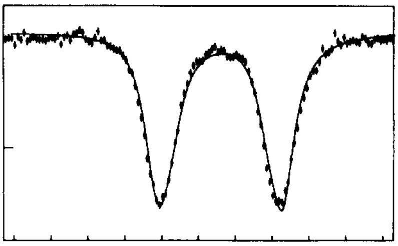

FIG. 5. Recoilles absorption spectrum of ^{155}Gd in $Sr_2Nd_7Gd(SiO_4)_6O_2$. The theoretical smooth curve was obtained by a least-squares computer program.

Figure 5 shows the Mössbauer spectrum of $Sr_2Nd_7Gd(SiO_4)_6O_2$. The selection of this compound for a Mössbauer effect study, using a Gd source, was based on the idea that magnetic ordering of the compounds, if such exists, should be caused by the Nd^{3+} ions, and that the Gd^{3+} will represent this behavior. Least-squares computer calculations could fit the experimental spectra without taking into account magnetic hyperfine interactions, indicating that the Gd^{3+} ions are paramagnetic at 4.2 K and that, as pointed out above, this then holds for the Nd^{3+} ions as well. The isomer shift (IS) and the electric field gradient (eq*Q*) derived from the spectra are 0.53(1) mm/sec, relative to the source, and 248 mHz, respectively. The IS value most probably reflects the more ionic character of Gd in apatite than in the metallic source. The eq*Q* observed must be due to an asymmetric electric environment on the Gd^{3+} in its crystallographic site.

Discussion

The compounds investigated in this work all show paramagnetic behavior at the temperature ranges (4.2–300 K) and magnetic fields (2–15 kOe) studied. Mössbauer effect data of $Sr_2Nd_7Gd(SiO_4)_6O_2$ have supported the lack of magnetic ordering in these compounds. μ_B values obtained for the higher temperature range of 80–300 K agreed well with the theoretical values, thus proving also the correctness of the chemical composition of the compounds. The Curie temperatures found (Table II) were all positive. This is usually an indication of ferromagnetism of the compounds; possibly at lower temperatures or higher field strengths that could have been proven. At the lower temperature range (4.2–40 K) the curves of $1/\chi$ vs T showed some deviation from a straight line. While this can be partly due to experimental difficulties in recording the very low temperatures, in the case of the Nd compounds, it might be attributed to crystal field effects. The existence of such an effect is indicated also by the deviation of the μ_B values of the Nd compounds from the theoretical values, such that μ_B values are lower than the theoretical ones.

Results obtained in this work, as well as results reported for the magnetic properties of Eu(II) apatites and of $Pb_6Nd_2Na_2(PO_4)_6Cl_2$, lead to the general conclusion that apparently apatites crystallizing in the $P6_3/m$ hexagonal structure do not tend to order magnetically above He temperature. The rare earth-containing phosphate and silicate apatites differ from each other in the distribution of the rare earth ions in their crystal structure. In silicate apatites the crystal structure determined (*5*) has shown that rare earth ions occupy all the 6*h* triangle sites and that they are located in the 4*f* column positions as well; in rare earth–lead apatites (*2*) with lower rare earth content, indications were found for a site preference of the 4*f* sites by the rare earth ions. In both types of apatites the shortest direct distance between the rare earth ions can be found in the column positions. In the case of $Sr_2Nd_8(SiO_4)_6O_2$, which has the smallest lattice constants among the compounds investigated, this bond length is 3.509 Å. This length is much smaller than 4.40 Å, the maximum *Ln–Ln* bond length for which ferromagnetic interactions have been found (*8*). The rare earth ions in the column positions are as a rule coordinated to nine oxygen atoms of the phosphate or silicate groups. It might well be that these oxygen atoms weaken the ferromagnetic coupling of the rare earth ions, since their contribution, by a superexchange, would act in the opposite direction, namely, by promoting antiferromagnetic ordering.

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