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Magnetic Susceptibilities of Cubic Mixed Europium Oxides

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The magnetic susceptibility χ of polycrystalline cubic solid solutions of Eu_2O_3 with Y_2O_3, and Gd_2O_3 have been measured. The χ of Eu^{3+} in $(Eu_xY_{1-x})_2O_3$ increases with decreasing concentration of Eu^{3+} ions, although the anisotropic exchange interaction would be expected to decrease at the same time. The χ of the smaller unit-cell compound, $(Eu_{0.1}Lu_{0.0})_2O_3$, yields an even higher value for the χ of Eu^{3+} than do the Eu-Y mixed oxides, indicating a strong dependence of the crystal-field parameters on the unit-cell dimension. In $(Eu_xGd_{1-x})_2O_3$ the χ of Eu^{3+} has the same value as in Eu_2O_2 for all values of x while the χ of Gd^{3+} is given by $\chi = C/[T+(1-x)\theta]$.

INTRODUCTION

The increased magnetic susceptibility χ of the Eu^{3+} ion in Eu_2O_3 as compared to its free-ion value[1] was interpreted recently by Huang and Van Vleck[2] in terms of the combined action of the crystalline field and anisotropic exchange. It has been assumed that the χ of the Eu^{3+} ion diluted by diamagnetic ions of Y^{3+} or Lu^{3+} should decrease at low concentrations of Eu^{3+} because of the decrease of the anisotropic exchange interaction between the Eu^{3+} ions. The present work shows that the χ of Eu^{3+} is increased at low concentrations of Eu^{3+} in the solid solutions of Eu-Y and Eu-Lu oxides, and remains almost unchanged at higher concentrations of Eu^{3+} in the Eu-Y oxides and at all concentrations of Eu^{3+} in the Eu-Gd oxides.

Huang and Van Vleck[2] were handicapped by insufficient experimental data on the dependence of the χ of Eu^{3+} on concentration, and it is to remedy this deficiency that the present work was undertaken at their suggestion.

The cubic rare-earth oxides crystallize in the bixbyite structure. There are two different sites for the metal ions; 75% occupy the asymmetric C_2 site, and the remainder occupy the more symmetric S site. The present work can be interpreted as indicating that the Eu^{3+} ions prefer the C_2 sites for low concentrations of Eu^{3+} in the mixed cubic oxides of Y and Lu.

EXPERIMENTAL PROCEDURE

The solid solutions $(Eu_xY_{1-x})_2O_3$ and $(Eu_xGd_{1-x})_2O_3$ with $x=0.2$, 0.4, 0.6, 0.8, as well as $(Eu_{0.1}Lu_{0.9})_2O_3$, were prepared by mixing the individual oxides in the same molar ratios as in the final product, and firing below the cubic-to-monoclinic phase-transition temperature of Eu_2O_3 (1100°C). The specimens were resintered and refined until single cubic phases were shown in sharp powder diffraction patterns, taken with a Guinier x-ray camera. The unit-cell dimensions measured from the above patterns conform to Vegard's law, as shown in Fig. 1. Single-cubic-phase specimens $(Eu_xLu_{1-x})_2O_3$ with x greater than 0.1 were not obtained, because of the large difference between the unit cells of the two pure oxides (10.87 and 10.39 Å).

The χ of the specimens was measured with a null coil pendulum magnetometer[3] between 95 and 295°K on samples weighing about 200 mg.

RESULTS AND DISCUSSION

The dependence of χ on the concentration x in $(Eu_xY_{1-x})_2O_3$ and $(Eu_{0.1}Lu_{0.9})_2O_3$ at 95°K is shown in Fig. 2. A similar variation of χ with x is obtained also at the other temperatures. It can be seen that the χ of Eu^{3+} is increased at low values of x and that the increase is more pronounced for the Eu-Lu than for the Eu-Y oxides.

The increased χ of the Eu^{3+} ion at small concentrations can be explained partly by supposing that the crystal field is much stronger at the C_2 than at the S_6 site, and that at low concentrations the Eu^{3+} ions occupy only the C_2 sites. The larger χ for small values of x was expected to be diminished by the decrease of anisotropic exchange interaction between the Eu^{3+} ions, but this is contradicted by our experimental data. It is also possible to assume that the crystal field is largely re-

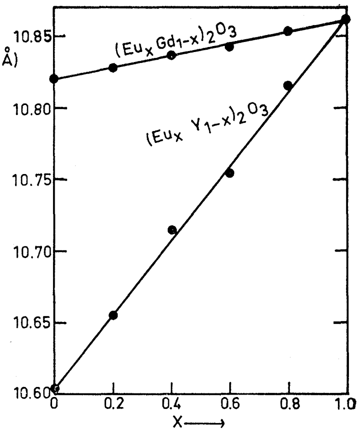

FIG. 1. Unit cell a versus concentration x of $(Eu_xY_{1-x})_2O_3$ and $(Eu_xGd_{1-x})_2O_3$.

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[3] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

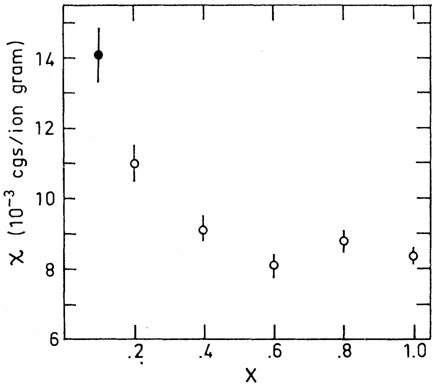

FIG. 2. Magnetic susceptibility χ per ion gram of Eu^{3+} versus concentration x of $(Eu_xY_{1-x})_2O_3$ (circle) and of $(Eu_{0.1}Lu_{0.9})_2O_3$ (dot) at 95°K.

sponsible for the increase, and that it is strongly dependent on the unit-cell dimensions. Indeed, this would agree with the finding of a larger χ for the Eu^{3+} ion in $(Eu_{0.1}Lu_{0.9})_2O_3$, which has a smaller unit cell [$a=10.44$ Å compared with $a=10.60$ Å for $(Eu_xY_{1-x})_2O_3$ compounds]. The χ of Eu^{3+} for $x=0.6$ is not markedly changed, presumably as a result of changes in the site occupation probabilities for Eu^{3+} and of increased unit-cell dimensions, compared to those in low-x compounds. The dependence of the crystal-field parameters on the unit-cell dimensions is further confirmed in the $(Eu_xGd_{1-x})_2O_3$ compounds, where χ of Eu^{+3} versus x is the same as in Eu_2O_3 because of the small difference in the unit-cell dimensions ($a=10.82$ Å and $a=10.87$ Å for pure Gd_2O_3 and Eu_2O_3, respectively, as compared with $a=10.61$ Å and $a=10.39$ Å for pure Y_2O_3 and Lu_2O_3, respectively).

The temperature dependence of χ for a concentrated ($x=0.8$) and a dilute ($x=0.2$) mixed Eu-Y oxide is shown in Fig. 3. The dependence of χ on the separation E_{10} between the levels $J=1$ and $J=0$ is given approximately by

$$\chi \sim [1-\exp(-E_{10}/kT)]E_{10}^{-1}.$$

Our assumption is that E_{10} is larger at lower concentrations than at the higher ones. This means that $\chi(95°K)/\chi(295°K)$ is larger at $x=0.2$ than at $x=0.8$, as indeed is shown in Fig. 3.

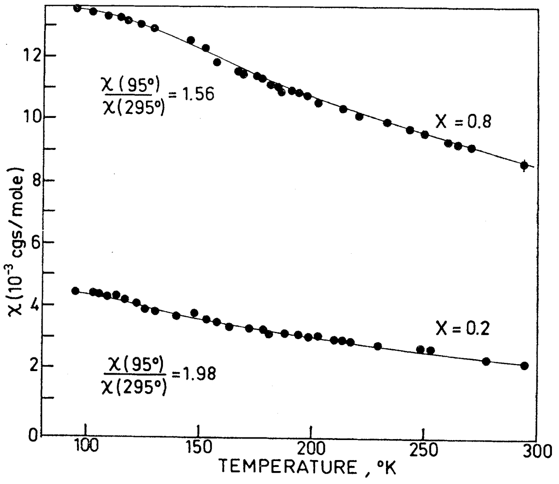

FIG. 3. Magnetic susceptibility χ per mole of compound versus temperature T of $(Eu_{0.2}Y_{0.8})_2O_3$ and $(Eu_{0.8}Y_{0.2})_2O_3$.

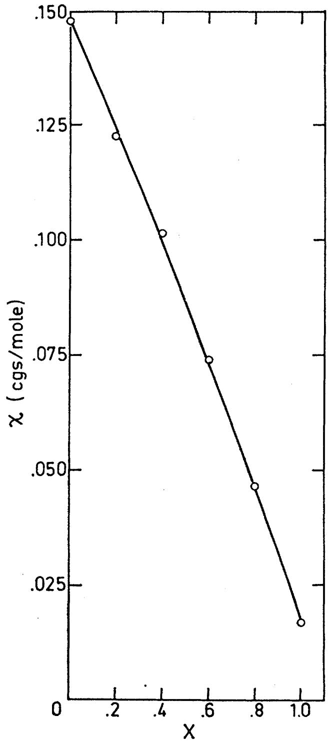

FIG. 4. Magnetic susceptibility χ per mole of compound versus concentration x of $(Eu_xGd_{1-x})_2O_3$ at 95°K: circle represents experimental; line represents calculated with $\chi=C/[T+(1-x)\theta]$.

The variation of χ of $(Eu_xGd_{1-x})_2O_3$ with x at 95°K is shown in Fig. 4. The same variation of χ with x is observed at all temperatures between 95 and 295°K. For $x=0$ the value of χ is found to be given by $C/(T+\theta)$, with $\theta=11$°K rather than the 18°K reported previously by Velayos.[4] Reexamining Velayos's data, it can be seen that $\theta=11$°K seems to fit his own χ at room and liquid-nitrogen temperatures better than $\theta=18$°K, which is obtained at high temperatures. The constant θ represents the strength of the antiferromagnetic interaction between the Gd^{3+} ions and is proportional to the concentration $(1-x)$ of Gd^{3+}. The χ of Gd^{3+} is given therefore by $X=C/[T+(1-x)\theta]$, in good agreement with the experimental results as shown in Fig. 4.

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