PHYSICAL REVIEW B VOLUME 1, NUMBER 5 1 MARCH 1970

Magnetic Susceptibilities of Cubic Mixed Europium Oxides

A. GRILL AND M. SCHIEBER
Department of Physics, Hebrew University of Jerusalem, Jerusalem, Israel

(Received 17 October 1969)

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-

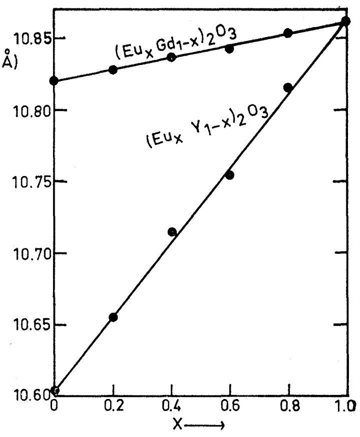

FIG. 1. Unit cell a versus concentration x of $(Eu_xY_{1-x})_2O_3$ and $(Eu_xGd_{1-x})_2O_3$.

---

[1] R. M. W. Trapness and P. W. Selwood, Nature **169**, 840 (1952).

[2] N. L. Huang and J. H. Van Vleck, J. Appl. Phys. **40**, 1144 (1969).

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

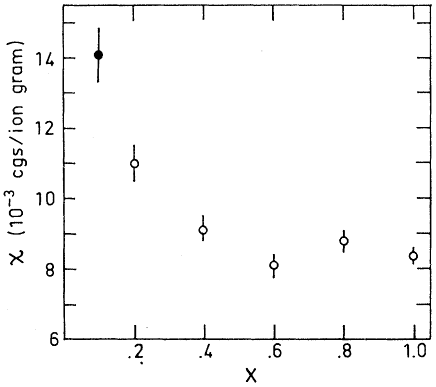

FIG. 2. Magnetic susceptibility χ per ion gram of Eu^{3+} versus concentration x of $(Eu_xY_{1-x})_2O_3$ (circle) and of $(Eu_{0.1}Lu_{0.9})_2O_3$ (dot) at 95°K.

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.

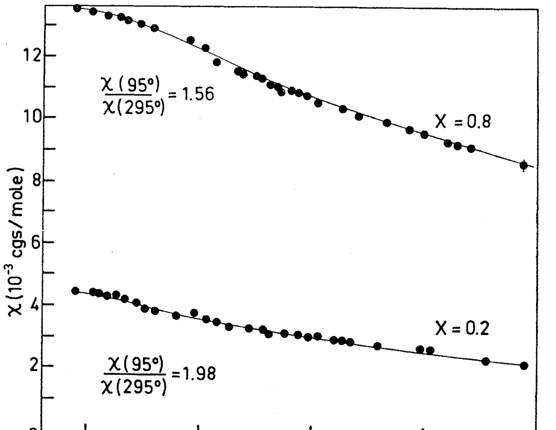

FIG. 3. Magnetic susceptibility χ per mole of compound versus temperature T of $(Eu_{0.2}Y_{0.8})_2O_3$ and $(Eu_{0.8}Y_{0.2})_2O_3$.

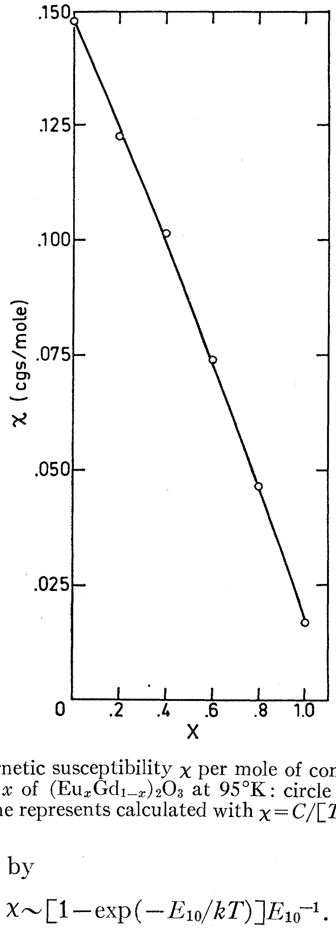

FIG. 4. Magnetic susceptibility χ per mole of compound versus concentration x of $(Eu_xGd_{1-x})_2O_3$ at 95°K: circle represents experimental; line represents calculated with $\chi=C/[T+(1-x)\theta]$.

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.

ACKNOWLEDGMENT

We would like to thank Professor J. H. Van Vleck for suggesting the subject and for valuable discussions of our experimental results.

---

[4] S. Velayos, Anales Real Soc. Fis. Quim. (Madrid) 33, 5 (1935).