EUROPIUM ORTHOSILICATE, A NEW TRANSPARENT FERROMAGNET*

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The known number of ionic compounds which become ferromagnetic is limited to only a few materials; among these are the recently discovered europium compounds.[1-4] This Letter reports the discovery of a new ferromagnetic europium compound which is optically transparent in the bulk. It has the composition Eu_2SiO_4 and, according to the usual silicate classification, would be called an orthosilicate.

The Eu_2SiO_4 powders, on which the initial magnetization measurements were made, were prepared by a solid-state reaction between EuO and SiO_2. These reactions were carried out in vacuo or under a hydrogen atmosphere at temperatures above 1200°C. The resulting product is a lemon-yellow powder which is insoluble in water and has no tendency to oxidize in air at room temperature. Subsequent magnetization and magneto-optical measurements were made on single-crystal specimens. These samples were platelike crystals with natural faces approximately 2-3 mm across and 0.05 to 0.1 mm thick.

The complete structure of Eu_2SiO_4 is not known, but Rau[5] has indexed it on an orthorhombic cell where $a = 9.71$ Å, $b = 49.56$ Å, and $c = 5.65$ Å with 28 formula units per cell. There appears to be layering along the direction of the b axis, and hence the true b parameter repeats every seven layers. The measured density of 6.74 g/cc is in good agreement with the theoretical value of 6.77 g/cc. The fact that Eu_2SiO_4 is an orthosilicate means that we have an assembly of discrete SiO_4 tetrahedra with Eu^{++} in the holes between them, probably in sixfold coordination. A crystal chemical comparison with the strontium silicates failed to yield any further structural information about Eu_2SiO_4, primarily because there seems to be some disagreement as to the structure of Sr_2SiO_4. Our x-ray powder data for Eu_2SiO_4 agrees with Toropov and Chih-Ch'iung[6] for Sr_2SiO_4 and not with O'Daniel and Tscheischwili[7] who originally looked at the structure of Sr_2SiO_4.

Two other europium silicates were found in the EuO-SiO_2 system which were isostructural with the strontium silicates. These were $EuSiO_3$ and Eu_3SiO_5, the latter being ferromagnetic below 4°K.

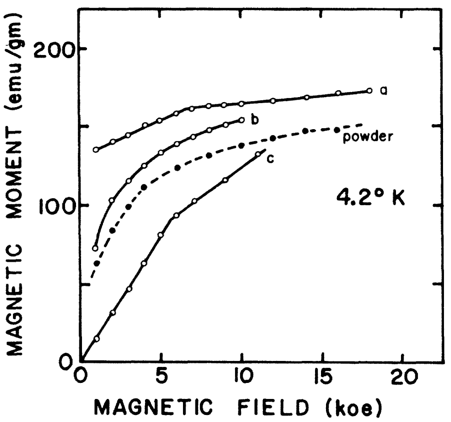

FIG. 1. Magnetic moment for Eu_2SiO_4 as a function of field at 4.2°K for a powder sample (dashed line) and three directions (a, b, and c) of a single crystal. Directions a and b are in the plane of the platelike crystal, and c is perpendicular to the plane.

The magnetic moments were measured by a force method over a temperature range 1.6°K to 300°K. Results for the powder and single-crystal Eu_2SiO_4 are given in Fig. 1 and Table I. The single crystal was in the platelike form described previously. Ferromagnetism is clearly indicated by the shape of the magnetization curves and from the positive θ intercept of the reciprocal susceptibility curve. Comparison of the theoretical and measured values of the molar Curie constant, C_M, and the magnetic moment at 0°K, M_0, show the average measured values to be 15% and 8% low for the powder and crystal, respectively. The low moments of these samples suggests the presence of trivalent europium which has $J = 0$ total angular momentum. The incorporation of trivalent europium in the orthosilicate structure is easily understood in terms of a solid solution

Table I. C_M is the molar Curie constant, θ and T_c are in degrees Kelvin (±1°K), the magnetic moment M (emu/g) is for 4.2°K at 20 000 Oe, M_0 is the estimated value at 0°K, and M_T is the theoretical value for stoichiometric Eu_2SiO_4 where all the europium is divalent.

Eu_2SiO_4	C_M	θ	T_c	M	M_0	M_T
Powder	6.60	7	···	150	170	197
Single crystal	7.01	7	≈7	175	184	197

between $Eu_4(SiO_4)_3$ and Eu_2SiO_4, since Toropov and Chih-Ch'iung[6] have shown that up to 20% rare earth orthosilicates, $RE_4(SiO_4)_3$, can dissolve in Sr_2SiO_4.

The magnetization curves (Fig. 1) indicate that Eu_2SiO_4 is quite anisotropic. The spins have an easy direction in the plane of the platelet and the in-plane anisotropy appears to be greater than 10^6 ergs/cc at 4.2°K, while the anisotropy perpendicular to this plane is even larger. The initial slope of the M-H curve for the perpendicular direction (curve c, Fig. 1) is due to demagnetization. If no crystalline anisotropy were present this line would intercept the easy direction of magnetization at something less than $4\pi M$.

Figure 2 shows the results of optical measurements made on Eu_2SiO_4 single-crystal platelets at room temperature. Verdet constant measurements are shown for the two mercury lines (5461 Å and 5770 Å) which were not greatly attenuated by the sample. The light beam and the magnetic field were directed perpendicular to the surface of the platelet. With a magnetic field of 3 kOe, rotations of approximately one degree were obtained from a crystal 65 μ thick. Our largest value of Verdet constant (at 20°C), -2.5 min/Oe-cm, is almost an order of magnitude larger than any other value previously reported. Absorption measurements made from 3000 Å to 8000 Å, also given in Fig. 2, show that the Faraday rotation is a strong function of photon energy near the absorption edge. At 77°K the rotation was observed to be about three times that at room temperature, which is in approximate agreement with the increase in magnetization. If the rotation remains proportional to the magnetization, for a saturation magnetization of 175 emu/g at 4.2°K, we would expect a rotation of 76 000 deg/cm. We have not yet made measurements of rotation in the liquid helium temperature region.

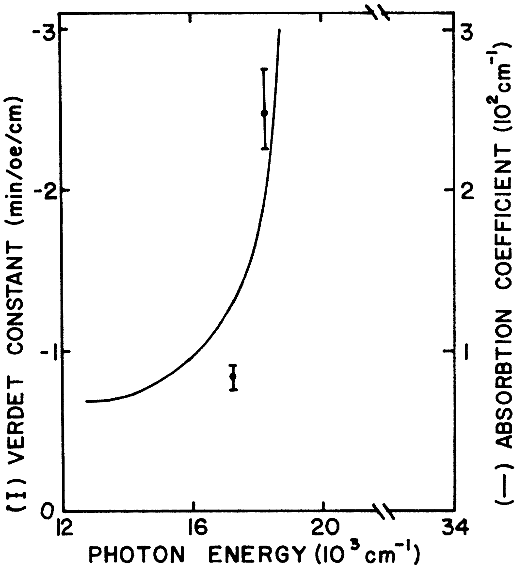

FIG. 2. Verdet constant and absorption coefficient at room temperature as a function of photon energy for Eu_2SiO_4.

If we compare the Curie temperature (7°) with the europium chalcogenide series,[2] Eu_2SiO_4 has about the same value as EuSe which has a nearest-neighbor Eu distance of 4.4 Å. Assuming sixfold coordination, we may infer from this that the nearest-neighbor europium distance in the silicate is similar.

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