The static magnetic susceptibilities of reduced rare earth halides were measured in the temperature range 10 – 300 K. It was found that the halides – examples of a series of condensed clusters – exhibit magnetic behaviour which varies with the degree of cluster condensation:

a) Compounds with isolated metal octahedra (e.g. TbI₃) show a tendency to ferromagnetic coupling and micromagnetic behaviour below 30 K.

b) Compounds with chains of metal octahedra (e.g. Tb₂Cl₆, GdBr₃) show Curie-Weiss behaviour and antiferromagnetic coupling below approx. 100 K.

c) Compounds with layers of metal octahedra (e.g. GdBr₃, CeBr₃) follow the Curie-Weiss law with only a small tendency to moment coupling (ferro- and antiferromagnetic) at low T.

Structural consequences of these moment couplings are discussed.

08.5-04 MAGNETIC PROPERTIES OF REDUCED RARE EARTH HALIDES. R.J. Reuterhaus and A. Simon, Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart, W-Germany

Many of the AK₂ compounds, where A and B are cations and an anion, have the ideal cubic perovskite structure, or structures which are slightly distorted from the ideal one (J.B. Goodenough and J.M. Longo, “Landolt-Börnstein”, edited by E.H. Nicolau and V. Wohlfarth, Berlin-Heidelberg, Germany, (1970) 1, 126). Some of these compounds have another feature which is crystallographic polymorphism, namely the existence of two different phases at a given temperature range. The compounds向きHnC₃ possess this feature of polymorphism.

The two phases obtained for HnC₃ at room temperature are: i) KD₄C₃ type structure (E. Gurevitz, A. Horowitz and K. Shaked, Phys. Rev. B, (1979) 20, 4544) and ii) CaTl₂ (distorted perovskite) type structure. The two phases obtained for KMnC₃ are i) hexagonal of a RbTiO₃ type structure (M. Helm, J. Makovsky and H. Shaked, Phys. Rev. B, (1971) 3, 821) and ii) ideal perovskite structure. These compounds were studied by neutron diffraction. A neutron diffraction study of phase (ii) in the two compounds has been carried out. Comparison between the two phases in the two compounds reveals the following:

In the two phases of KMnC₃, the Mn²⁺ ions occupy octahedral sites. These octahedra are formed by the Ga²⁺ ions and are highly distorted in the KMnC₃ type phase while almost ideal in the perovskite type phase. The octahedra are differently packed in the two phases. In the KMnC₃ type they share a common edge, forming zigzag chains and in the perovskite type phase they share a common vertex. The two phases have four formula units per unit cell and almost the same unit cell volume: 8.73x7.08x9.57=490.86 Å³ for the KMnC₃ type and 7.08x9.97=712.70 Å³ for the distorted perovskite type.

The structure of the two phases belong to D₃h – Pbnm but there is not a simple transformation between the two structures. The two phases are paramagnetic at room temperature and undergo at low temperature a transition to antiferromagnetic state. The Neel temperature of the KMnC₃ type is 2.1 K. Below this temperature it has a spiral magnetic structure with amplitude of 3.6 µB. The Neel temperature of the distorted perovskite type is 102 K below which it has a G-type magnetic structure with 4.6 µB per Mn²⁺ ion. A transformation between the two phases of KMnC₃ can be obtained by rotating every second cube along one of the three fold axes (cube diagonal) by 180° around this axis. Such a transformation does not alter the structure of the planes perpendicular to this axis. The ideal perovskite structure has one formula unit per unit cell, the dimensions of which are (5.09) x(131.87) Å. The hexagonal structure consists of six formula units per unit cell of the dimensions 7.16x7.16x5.16x17.81x79.04 Å³ which corresponds to 132.01 Å³ per formula unit. The two phases are paramagnetic at room temperature and undergo at low temperature a transition to antiferromagnetic state. The Neel temperature of the hexagonal phase is 94 K. Below this temperature each magnetic moment in the planes perpendicular to the six fold axis is antiferromagnetically coupled to its nearest neighbours in the planes and in the adjacent planes. The magnetic moment of the Mn²⁺ ions is 4.1 µB. The Neel temperature of the perovskite phase is 107 K. Below this temperature the magnetic structure of each plane perpendicular to a three fold axis is the same as in the hexagonal phase. These planes are antiferromagnetically coupled to form a G-type magnetic structure with 5 µB per Mn²⁺ ion.