

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

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:

- Compounds with isolated metal octahedra (e.g.  $Tb_7I_{12}$ ) show a tendency to ferromagnetic coupling and mictomagnetic behaviour below 30 K.
- Compounds with chains of metal octahedra (e.g.  $Tb_2Cl_3$ ,  $Gd_2Br_3$ ) show Curie-Weiss behaviour and antiferromagnetic coupling below appr. 100 K.
- Compounds with layers of metal octahedra (e.g.  $GdBr$ ,  $CeBr$ ) 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.

**08.5-05** MAGNETIC PROPERTIES AND PHASE TRANSITIONS OF  $TmAl_xGa_{2-x}$  ( $x = 0-2$ ).

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$RAI_2$  (R = rare earth) crystallize with cubic structure of  $MgCu_2$  type (Laves phase) and order predominantly ferromagnetic (W.E. Wallace, Rare Earth Intermetallics, Academic Press, New York (1973) p. 35 and 76). On the other hand antiferromagnetic  $RGa_2$  occurs mostly with hexagonal  $AlB_2$  type structure.  $TmGa_2$  and  $LuGa_2$  are both orthorhombic. Many other compounds of Al and Ga are isostructural (K. Girgis, Monatsh. Chem. 101 (1970) 721).

We determined the influence of Ga substitution of Al in  $TmGa_2$  on crystal structure and magnetic properties.

Two phases exist in the composition range of  $TmAl_xGa_{2-x}$ . The orthorhombic phase exists over a range of  $x=0.3$  to 2.0, the  $MgCu_2$  phase from  $x=0.0$  to 1.0.

The cell constants are:

$TmGa_2$	$a = 4.21 \text{ \AA}$	$b = 6.90 \text{ \AA}$
	$c = 8.08 \text{ \AA}$	
$TmAl_2$	$a = 7.77 \text{ \AA}$	

The crystallographic and magnetic structure determinations are in progress. A comparison of these results with those of  $(Ho, Al)Al_xGa_{2-x}$  will be presented. (K. Girgis and P. Fischer, AF-SSP 112 (1979) 11.

**08.5-06** CRYSTALLOGRAPHIC POLYTYPOISM AND MAGNETIC STRUCTURE OF  $KMnCl_3$  and  $RbMnCl_3$  - A NEUTRON DIFFRACTION STUDY. By E. Gurewitz, M. Melamud, A. Horowitz and H. Shaked, Nuclear Research Center-Negev, P.O.B. 9001, Beer-Sheva, Israel.

Many of the  $ABX_3$  compounds, where A and B are cations and X 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 K.H. Hellwege, Springer-Verlag, Berlin-Herdelberg, Germany, (1970) 4, 126). Some of these compounds have another feature which is crystallographic polytypism, namely the existence of two different phases at a given temperature range. The two compounds  $KMnCl_3$  and  $RbMnCl_3$  possess this feature of polytypism.

The two phases obtained for  $KMnCl_3$  at room temperature are: i)  $KCdCl_3$  type structure (E. Gurewitz, A. Horowitz and H. Shaked, Phys. Rev. B, (1979) 20, 4544) and ii)  $CaTiO_3$  (distorted perovskite) type structure. The two phases obtained for  $RbMnCl_3$  are i) hexagonal of the  $BaTiO_3$  type structure (M. Melamud, J. Makovsky and H. Shaked, Phys. Rev. B (1971) 3, 821) and ii) ideal perovskite structure. These compounds were studied by neutron diffraction. The neutron diffraction studies of phase (i) in the two compounds have already been reported (Gurewitz et al, Melamud et al). 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  $KMnCl_3$  the  $Mn^{2+}$  ions occupy octahedral sites. These octahedra are formed by the  $Cl^-$  ions and are highly distorted in the  $KCdCl_3$  type phase while almost ideal in the perovskite type phase. The octahedra are differently packed in the two phases. In the  $KCdCl_3$  type they share a common edge, forming zig-zagging 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:  $8.77 \times 3.88 \times 14.42 = 490.68 \text{ \AA}^3$  for the  $KCdCl_3$  type and  $6.98 \times 7.08 \times 9.97 = 492.70 \text{ \AA}^3$  for the distorted perovskite type. The structure of the two phases belong to  $D_{2h}^{15}$  - 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  $KCdCl_3$  type is 2.1 K. Below this temperature it has a spiral magnetic structure with amplitude of  $3.8 \mu_B$ . The Neel temperature of the distorted perovskite type is 102 K below which it has a G-type magnetic structure with  $4.6 \mu_B$  per  $Mn^{2+}$  ion.

A transformation between the two phases of  $RbMnCl_3$  can be obtained by rotating every second cube along one of the three fold axes (cube diagonal) by  $180^\circ$  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  $(5.09)^3 = 131.87 \text{ \AA}^3$ . The hexagonal structure consists of six formula units per unit cell of the dimensions  $7.165 \times 7.165 \times \sin 60^\circ \times 17.815 = 792.04 \text{ \AA}^3$  which corresponds to  $132.01 \text{ \AA}^3$  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  $Mn^{2+}$  ions is  $4.1 \mu_B$ . The Neel temperature of the perovskite phase is 102 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  $5 \mu_B$  per  $Mn^{2+}$  ion.