

## Neutron Diffraction Study of the Magnetic Structure of Alpha-Phase Chromia-Alumina Solid Solutions

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The Néel temperatures of alpha-phase chromia-alumina solid solutions, measured by powder neutron diffraction methods, decrease with decreasing chromia content, reaching an extrapolated value of zero degrees Kelvin at  $33 \pm 2$  mole % chromia.

### Introduction

The Néel temperatures,  $T_N$ , of alpha phase chromia-alumina solid solutions have been measured by Knappwost and Gunsser (1), Foner (2) and Poole and Itzel (3), using electron spin resonance (1), (3) and antiferromagnetic resonance (2) methods. Though Knappwost and Gunsser (1) and Foner (2) have studied only high-chromia alloys, Poole and Itzel (3) have examined alloys over the entire composition range. Poole and Itzel (3) found  $T_N$  to be approximately directly proportional to the mole fraction of  $\text{Cr}_2\text{O}_3$ , but for  $\text{Cr}_2\text{O}_3$  concentrations below about 50 mole %,  $T_N$  became broad and ill-defined.

In this work chromia-alumina solid solutions have been studied by powder neutron diffraction methods.

### Experimental

Poole and Itzel (3) prepared specimens by calcining the coprecipitated hydrated oxides for 24 h at  $1400^\circ\text{C}$ . Our samples were made by heating the coprecipitated hydrated oxides at  $900^\circ\text{C}$ , pulverizing in an agate mortar, washing, reheating to  $900^\circ\text{C}$  and repulverizing. Cylindrical samples approximately 1-cm diam  $\times$  1.5-cm long and 70% theoretical density were produced by pressing these powders at 20 tons in.<sup>-2</sup> and sintering at  $1500^\circ\text{C}$ .

Powder X-ray diffraction lines from these compacts were sharp and no lines apart from those of the alpha phase were observed. The lattice parameter variation with the mole fraction of  $\text{Cr}_2\text{O}_3$  approximately obeyed Végard's law as was found in the more detailed work of Graham (4). The samples were analysed by X-ray fluorescence methods.

The onset of antiferromagnetism was shown by the enhancement of the (012) and (014) (indexed on a hexagonal unit cell) neutron diffraction peaks on cooling the samples (5), (6). The intensity of the (012) peak, chosen because of its greater intensity, was monitored by setting the counter at the peak position, and heating or cooling the sample at a rate of less than  $1 \text{ deg min}^{-1}$ , especially at temperatures near  $T_N$ . The angular resolution was such that changes of the Bragg angle with temperature were insignificant; the increase of the diffuse scattering when the sample was heated above  $T_N$  [paramagnetic scattering (7)] was found to be not significant within our experimental accuracy. The magnetic moment per Cr atom at  $0^\circ\text{K}$  was calculated by intercomparison of the magnetic and nuclear intensities; the positional parameters of Newnham and de Haan (8) were used to calculate the relative nuclear intensities and the  $\text{Mn}^{++}$  form factor was used for the magnetic scattering, as was done by Corliss et al., (6) in their work on pure  $\text{Cr}_2\text{O}_3$ . The Debye-Waller factor was ignored.

### Results and Discussion

Results for the composition dependence of  $T_N$  and the moment per Cr atom at  $0^\circ\text{K}$  are shown in Figs. 1 and 2, respectively.

Our results for  $T_N$  agree with those of the other workers at compositions above about 50 mole %  $\text{Cr}_2\text{O}_3$ . In addition, the increased sensitivity of neutron diffraction over the electron spin resonance method has enabled the curve of  $T_N$  versus composition to be confidently extended below 50 mole %  $\text{Cr}_2\text{O}_3$ . However, the results shown in Fig. 2 for the composition dependence of the moment per Cr

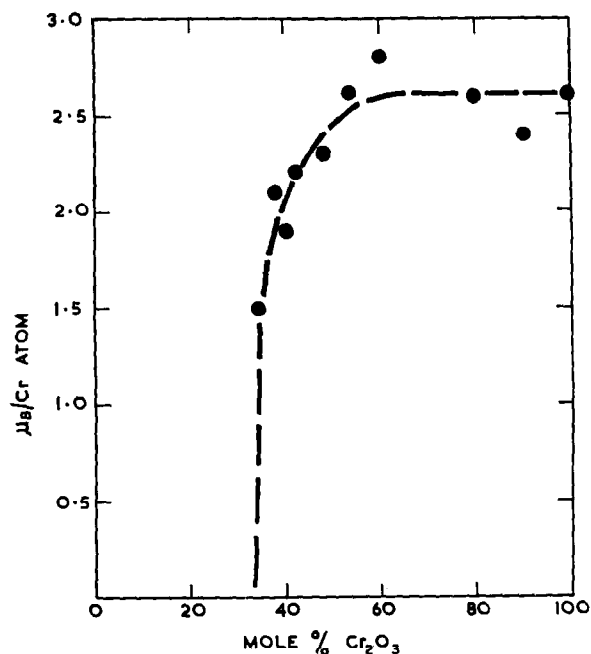


FIG. 1. Dependence of Néel point of chromia-alumina alloys on composition. The results of other workers are also shown. The estimated errors in our results are  $\pm 10^\circ\text{K}$  for the Néel points and  $\pm 2$  mole % for the compositions.

atom suggest that the magnetic transformation becomes less cooperative for  $\text{Cr}_2\text{O}_3$  contents below about 50 mole % as found by Poole and Itzel (3).

The approximately linear variation of the lattice parameters with the mole fraction of  $\text{Cr}_2\text{O}_3$  indicates that the Cr and Al atoms are approximately randomly distributed over the available metal atom sites, in agreement with the results of McCauley and Gibbs (9).

The problem of diluting a localized-moment type of magnetic material with nonmagnetic atoms has been discussed by several authors (10)–(15). Theoretical values of the limiting concentration,  $C_0$ , of magnetic ions at which antiferromagnetism at  $0^\circ\text{K}$  disappears, depend on the spin,  $S$ , per magnetic ion and the coordination number,  $Z$ , of each magnetic ion. Smart (13) gives

$$C_0 = (Z - 1)^{-1}, \quad (1)$$

whereas Elliott (14) gives a formula which for  $S = 3/2$  reduces to

$$C_0 \approx 2(Z - 1)^{-1}. \quad (2)$$

Elliott and Heap (15) give  $C_0$  values for simple cubic and body-centred cubic lattices as 0.21 and 0.15, respectively; these values very nearly satisfy

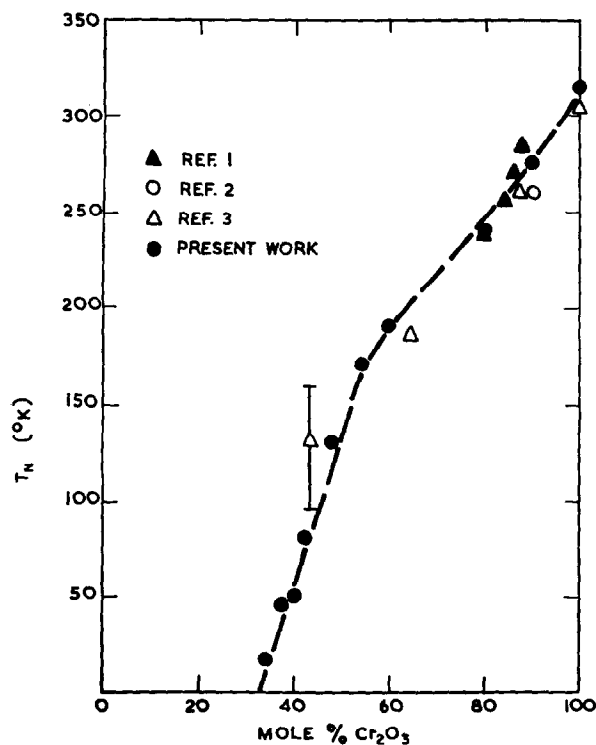


FIG. 2. Dependence of antiferromagnetic moment per Cr atom of chromia-alumina alloys on composition. The estimated errors are  $\pm 0.2 \mu\text{B}$  for the Bohr magneton numbers and  $\pm 2$  mole % for the compositions.

Eq. (1). Smart (13) and Elliott and Heap (15) have also given theoretical curves for the variation of the Néel point with the concentration of magnetic ions; although our curve in Fig. 1 is qualitatively in agreement with these curves, precise comparison cannot be made because of the uncertainty in the coordination number appropriate to chromia-alumina (see below).

By experiment we find  $C_0 \simeq 1/3$  (Fig. 1) and substitution into Eqs. (1) and (2) yields  $Z \simeq 4$  and 7, respectively. However, such a procedure assumes a *completely* random distribution of Cr and Al atoms over the available metal atom sites and ignores the changes of the appropriate superexchange interactions due to the dependence of the interatomic distances on composition. It is very difficult to calculate an effective  $Z$  on physical grounds.

Pratt and Bailey (16) have discussed the magnetic structure of  $\text{Cr}_2\text{O}_3$  in terms of strong magnetic interactions between nearest-neighbour Cr pairs on the  $c$  axes with a weak molecular field to describe the interactions with the other Cr atoms in the crystal. Their explanation is consistent with the nonzero  $C$  direction magnetic susceptibility of  $\text{Cr}_2\text{O}_3$  at  $0^\circ\text{K}$  and observations that the antiferromagnetic moment per Cr atom at  $0^\circ\text{K}$  is not  $3 \mu\text{B}$  as expected for a  $\text{Cr}^{+++}$  ion [Corliss et al., (6) found a value of  $2.76 \pm 0.03 \mu\text{B}$ ; the less precise results shown in Fig. 2 gave  $2.6 \pm 0.2 \mu\text{B}$ ].

However, they predicted an ordered canting of the  $\text{Cr}^{+++}$  spins which was proved incorrect by the subsequent neutron diffraction experiments of Corliss et al., (6). In addition, Pratt and Bailey (16) do not appear to have considered the intrinsic lowering of the antiferromagnetic moment per atom due to zero-point magnon fluctuations. For a simple cubic material [ $Z = 6$  which is intermediate between the values predicted by Eqs. (1) and (2)],

Kittel (17) gives  $\Delta S_z$ , the lowering of the antiferromagnetic sublattice magnetisation at  $0^\circ\text{K}$  due to zero point fluctuations, as  $\Delta S_z = 0.078$  per atom, i.e.,  $0.16 \mu\text{B}/\text{atom}$ .

Within our experimental accuracy, we have detected no modulation of the diffuse scattering at low  $\text{Cr}_2\text{O}_3$  concentrations which would be characteristic of short-range magnetic order. There will be very little crystal disorder scattering because of the similarity of the nuclear scattering lengths of Cr and Al.

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