



ultra-violet absorption at $\lambda = 2700 \text{ \AA}$. At this wavelength, phenol absorbs about 330 times as strongly as benzene, so that it is possible to detect the production of quite small amounts ($5 \times 10^{-7} \text{ gm./c.c.}$). With a quarter-saturated solution of benzene water, the increase in extinction coefficient is about four-fold for a dose of 5,000 r. and about twenty-fold for a dose of 25,000 r. (see graph). In this dose-range, measurements can be reproduced within ± 3 per cent. The method is less sensitive than that employing the Folin-Ciocalteu reagent; but for doses greater than 5,000 r. it has been possible to obtain more consistent results with much less trouble.

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¹ Day, M. J., and Stein, Gabriel, *Nature*, **164**, 671 (1949).

Changes of Crystal Structure in Antiferromagnetic Compounds

A RECENT communication by Selma Greenwald and J. S. Smart¹ has directed attention to the significance of the structural deformations observed by us in monoxides of the transition elements² in relation to their antiferromagnetic behaviour. It is particularly noteworthy that the temperatures at which departure from the high-symmetry face-centred cubic structure cell is first manifest are almost exactly the antiferromagnetic Curie temperatures. It would appear that deformations of the simpler arrangements existing above these Curie temperatures are a natural consequence of the setting of adjacent magnetic atoms in anti-parallel spin orientations below these temperatures. Neutron diffraction work on manganous oxide by Shull³ has shown that the magnetic cell has a lattice constant double that of the elementary structure cell; but it remains for X-rays to demonstrate the change in shape consequent upon the preferential arrangement of the metal atoms.

Greenwald and Smart have determined, more exactly than we have done, the temperature at which tetragonal symmetry is assumed by cobalt monoxide. The temperature coincides with the antiferromagnetic Curie temperature. Moreover, they find that chromium sesquioxide, Cr_2O_3 , which is an antiferromagnetic substance, exhibits anomalous changes in the structure cell dimensions, on cooling through the temperature at which large variations in magnetic susceptibility are found.

We can now add to the list the face-centred cubic form of manganous sulphide, MnS . Powder photographs with iron radiation of manganous sulphide at liquid-air temperature show splitting or multiplicity of such high-order reflexions as 420 and 422 but not of 400. A deformation of the face-centred cubic cell has therefore occurred on cooling, of the same kind as that found for nickelous oxide and manganous oxide—that is, such that rhombohedral symmetry is assumed. Departure from the cubic arrangement is appreciable at 95° K. , and hence may well commence during cooling through the antiferromagnetic Curie temperature of 165° K. ⁴; no deformation is noticeable at 200° K.

A further observation on ferrous oxide may also be reported. It is well known that the composition departs more or less from stoichiometric proportions according to the method of preparation, but is always deficient in iron with respect to FeO . We have found that the magnitude of the rhombohedral deformation from face-centred cubic symmetry is related to composition. At any given temperature, the deformation is greater for the least iron-deficient oxide than for an oxide of relatively low iron content. For example, we find that, at 95° K. , the structure cell of the oxide most closely approaching FeO has a rhombohedral angle of $59^\circ 32'$, whereas for an oxide much more deficient in iron the rhombohedral angle is $59^\circ 55'$ (compared with 60° when there is no deformation from face-centred cubic symmetry).

Now, the concentration of iron atoms is greatest when the ferrous oxide is least iron-deficient. Consequently, at a given temperature, it might be expected that the influence of the exchange interactions on the effective potential energy of the magnetic atoms would be largest for the least iron-deficient oxide. It follows that, as the iron-deficiency increases, the antiferromagnetic Curie temperature should decrease, and the structural deformation at a given lower temperature should become less. In respect of the magnitude of structural deformation the expectations are confirmed by the above observations, and it would be interesting to have, as well, direct measurements of the antiferromagnetic Curie temperatures for ferrous oxides of different compositions.

It may be added that, although the structure cell decreases in size as the oxide becomes more iron-deficient, apparently such decrease by no means offsets the effect of the lower concentration of iron atoms.

Some evidence has been obtained that variations of a similar kind occur with manganous oxide.

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¹ Greenwald, S., and Smart, J. S., *Nature*, **166**, 523 (1950).

² Tombs, N. C., and Rooksby, H. P., *Nature*, **165**, 442 (1950).

³ Shull, C. G. (private communication, April 1950).

⁴ Bizette, H., and Tsai, B., *Bull. Soc. chim. France*, D 531 (1949).