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MAGNETIC STRUCTURES IN THE IRON-GERMANIUM SYSTEM

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Three phases in the iron-germanium system have been investigated by neutron diffraction for determining their atomic and magnetic structures. Of these, $FeGe_2$ is found to be antiferromagnetic with a Néel temperature of 315°K and $Fe_{1.67}Ge$ is ferromagnetic having a Curie temperature of 510°K. There is evidence of a distortion of the ideal "filled" NiAs structure in the case of the latter. FeGe is paramagnetic down to 140°K.

STUDY of binary alloys of the iron series transition metals with elements of IVB and VB groups is interesting because of their pronounced covalent character which allows interpretation in terms of Pauling's concept of hybridization of the s-d and s-p orbitals and their mutual overlap.

The present study which is one of a series of neutron diffraction investigations being carried out at Trombay using a diffraction spectrometer at the Canada India Reactor concerns three phases in the iron-germanium system, namely $FeGe_2$, FeGe and $Fe_{1.67}Ge$. The available magnetization data indicated that $FeGe_2$ [1] is antiferromagnetic with a Néel temperature of 190°K while $Fe_{1.67}Ge$ [2] is ferromagnetic with a Curie temperature of 485°K. An antiferromagnetic structure for FeGe was proposed by Ohoyama et al.[3] on the basis of magnetization data.

The alloys were prepared using spectrographically pure iron and germanium. In the case of $FeGe_2$, after outgassing at 1070°K, the iron sponge was mixed with the right proportion of germanium and heated in a magnesia crucible to 1670°K. The crucible was held at this temperature for 30 min and then the temperature was lowered slowly. The specimen was furnace cooled below 1070°K. $Fe_{1.67}Ge$ was prepared by melting the required proportions of iron and germanium using an alumina crucible in an induction furnace. The melt was thoroughly agitated to ensure homogeneity and then cooled in the furnace. Some free iron was detected in the X-ray powder photograph of $Fe_{1.67}Ge$ which was confirmed by chemical analysis. In the case of FeGe, compacted iron powder and germanium in the correct proportions were taken in an alumina crucible and maintained at 1330°K for 30 min in an induction furnace. The specimen was then cooled in the furnace after annealing at 970°K for 240 hr.

$FeGe_2$ has a tetragonal, 14/mm structure. The X-ray film gave lattice spacings of a = 5.90 Å and c = 4.94 Å in good agreement with the published values. The atom positions are indicated in Fig. 1. The x-parameter for the germanium positions was determined to be 1/6 by noting the absence of (110) type of reflections in the X-ray photograph. The room temperature neutron diffraction pattern showed normal lattice reflections and intensities agreed to within 5 per cent with the calculated intensities. The diffraction pattern at 145°K, shown in Fig. 2 (along with a pattern taken at room temperature) showed extra reflections corresponding to the indices (100), (210) and (101) which are magnetic and arise from an antiferromagnetic structure as suggested in a preliminary report.[4] Temperature dependence of the (100) intensity indicated a Néel temperature of 315°K. Saturation intensities of (100) and (210) show that the magnetic moment per iron atom is $1.2 \pm 0.1 \mu_B$ and that the moments lie within the basal planes. The magnetic cell has the same a as the chemical cell but c half as long. The moments within a (200) plane are parallel but alternate (200) planes are arranged antiferromagnetically. The relative orientation of moments is indicated in Fig. 1. This leads to a first neighbor ferromagnetic interaction while the second and third neighbors are antiferromagnetic. This is plausible because

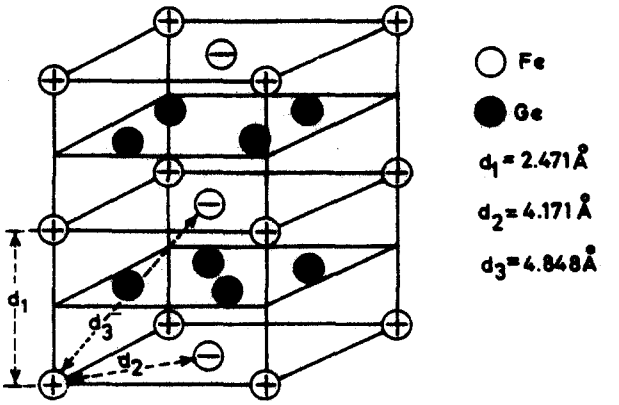

FIG. 1

The unit cell of $FeGe_2$ showing interatomic distances and the relative spin orientations. The coordinates of equivalent positions are (0, 0, 0; ½, ½, ½)+. The positions of atoms are:

Fe at 4a 0, 0, 0 0, 0, ½

Ge at 8h x, ½ + x, ¼
$\bar{x}$, ½ - x, ¼
½ + x, $\bar{x}$, ¼
½ - x, x, ¼

the first neighbors are at a distance of 2.47 Å apart which is the same as in metallic iron and a direct ferromagnetic exchange between them is dominant. In the case of second and third neighbors, their distances are too large for a significant direct overlap but there is indirect exchange via the hybridized s-p orbitals of the germanium atoms which lie at a distance of 2.52 Å. The bond angles for the interaction are respectively 113° and 148° which suggest strong superexchange interaction. The magnetic moment of 1.2 μ_B per iron atom arises from the hybridization of the 3d and 4s orbitals of the iron atoms owing to the tetragonal crystalline field surrounding them. These results are in agreement with those of Krén and Szabó[5].

$Fe_{1.67}Ge$ has been reported to belong to the hexagonal, P63/mmc space group.[2, 6] But the systematic absence of intensities like (112), (004) and (114) in the neutron diffraction pattern clearly ruled out the ideal "filled" NiAs structure. This structure also predicts (102) and (110) intensities to be almost equal. But the shape of the observed peak in the neutron diffraction pattern indicated a single reflection which was confirmed by X-ray examination using Co-Kα radiation. The observed intensities suggest distortion in the x as well as the z parameters

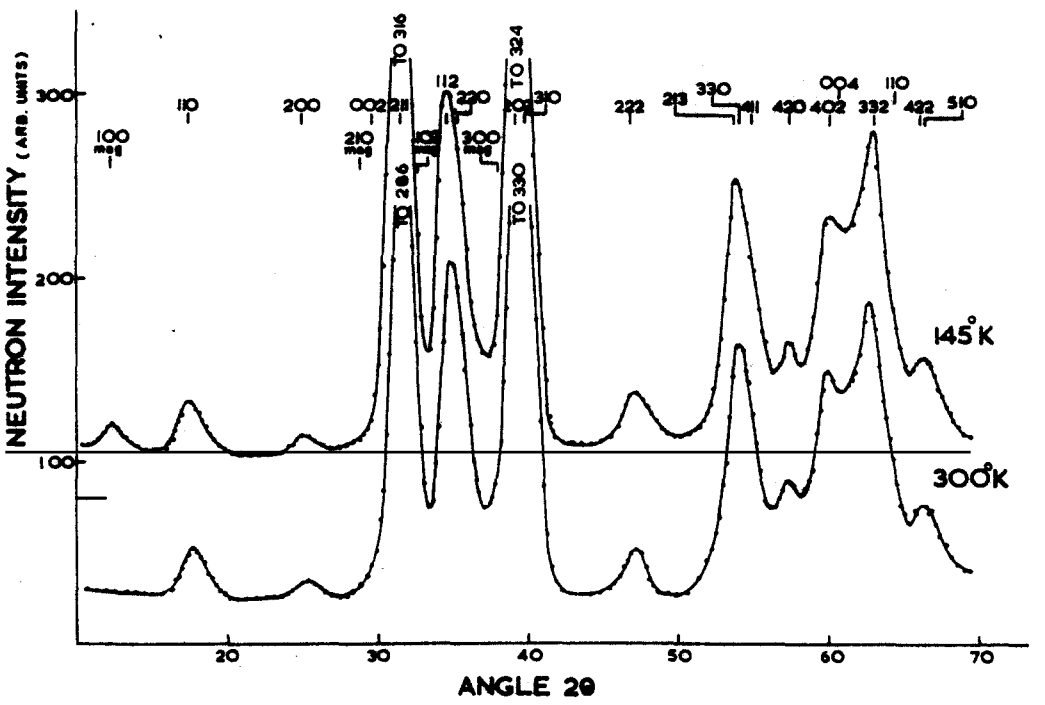

FIG. 2

The neutron diffraction pattern of $FeGe_2$ at 145° and 300°K. (λ = 1.27 Å)

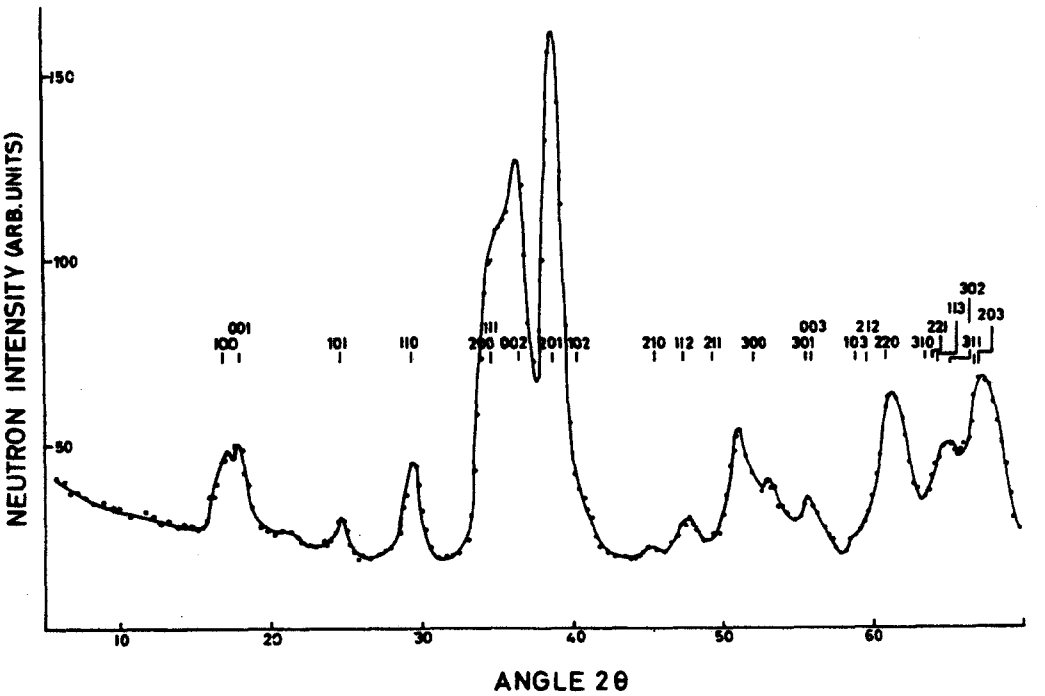

FIG. 3

The neutron diffraction pattern of FeGe at 300°K. (λ = 1.27 Å)

which are being determined. The present analysis indicates that the possible space groups are $P6_3mc$, $P\bar{6}2c$, $P6_3/mmc$. It may be mentioned here that neutron diffraction intensities in the case of $Mn_{1.74}Sn$ showed that it does have the ideal "filled" NiAs structure.[7] The absence of extra reflections in $Fe_{1.67}Ge$ below the Curie temperature indicated a magnetic cell of the same size as the chemical cell. The temperadependence of (100) reflection which is almost entirely magnetic gave a Curie temperature of 510°K. The magnetic origin of (100) reflection was confirmed by the application of a magnetic field along the (100) direction which appears to be an easy direction of magnetization, in agreement with the unpublished results of Forsyth and Brown. The intensity of (100) reflection gave magnetic moments of about 2 and 1 μ_B for the two iron atoms. In order to assign these moments specifically to the two iron sites more magnetic intensities have to be determined.

The neutron diffraction patterns of FeGe showed no magnetic Bragg reflections between 140° and 410°K. Figure 3 shows a pattern taken at room temperature which corresponds in detail to those taken at 140°K except for the temperature factor. Further, the paramagnetic scattering does not indicate a large magnetic moment of 3.1 μ_B per iron atom as suggested by Ohoyama et al.[3] The moment is rather of the order of 1.0 μ_B per iron atom. The space group P6/mm suggested by the same authors predicts the intensity of (112) to be about 80 per cent of that of (110) in the powder diffraction pattern as against the observed ratio of 40 per cent. This suggests a distortion in the z coordinates. The possible space group is P6/mm. Further investigations at low temperatures are being carried out.

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Trois phases dans le fer-germanium système ont été examinés par neutron diffraction pour déterminer les structures atomique et magnétique. Ceux-ci $FeGe_2$ est anti-ferromagnétique et à une Néel température de 315°K, $Fe_{1.67}Ge$ est ferromagnétique et à une Curie température de 510°K. Il y a évidence d'une distortion de la hexagone structure idéal dans $Fe_{1.67}Ge$. FeGe est paramagnétique jus qu'à 140°K.