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MAGNETIC ORDERING AND MAGNETIZATION IN AMORPHOUS Fe-Ge FILMS

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Résumé. — Des couches minces amorphes d'alliages Fe-Ge dont la composition varie de 0 à 75 at. % de Fe ont été préparées, le germanium se comportant comme une matrice diamagnétique amorphe pour les atomes de Fe. L'analyse des diagrammes de diffraction électronique montre que les couches sont amorphes pour toutes les concentrations, une interprétation est donnée en utilisant un modèle de sphères rigides. La conductivité électrique a été mesurée de 20 K à 300 K ; pour tous les films jusqu'à environ 25 at. % de Fe, la loi de Mott

$$\sigma(T) = \sigma_0 \exp - \left(\frac{T_0}{T} \right)^{1/4}$$

est vérifiée.

Des mesures magnétiques ont été réalisées pour établir la nature des interactions magnétiques. Un ordre magnétique à longue distance (ferromagnétique) apparaît pour une concentration critique d'environ 25 at. % de Fe. La température de Curie T_c croît très rapidement avec la quantité de fer au voisinage de la concentration critique. Les cycles d'hystérésis mesurés par effet Kerr sont rectangulaires, ce qui suppose une aimantation relativement uniforme des films. La concentration critique de percolation des atomes magnétiques implique un nombre de coordination d'environ 8 à cette concentration. Des mesures en microscopie Lorentz ont aussi été effectuées.

Abstract. — Amorphous thin films alloys of Fe-Ge ranging from 0 to 75 at. % iron have been prepared in which germanium serves as an amorphous diamagnetic matrix for iron atoms. Analysis of electron diffraction rings show the films to be amorphous for all compositions and can be interpreted on the basis of hard sphere models. Electrical conductivity from 20 K to 300 K has been performed, and for all films up to 25 at. % Fe, the Mott power law

$$\sigma(T) = \sigma_0 \exp - \left(\frac{T_0}{T} \right)^{1/4}$$

is obeyed.

Magnetic measurements have been performed to establish the nature and range of magnetic interactions.

Long range magnetic order (ferromagnetic) appears at around a critical concentration of about 25 at. % Fe. Curie temperature as a function of increasing Fe concentration shows extremely rapid increase of T_c around the critical concentration. The hysteresis loop measured by Kerr effect is square and implies uniform magnetization in the films. The critical percolation concentration of magnetic atoms implies a coordination number of ~ 8 for the amorphous matrix at this concentration. Measurements by Lorentz electron microscopy are also performed.

1. Introduction. — In recent years, a number of amorphous ferromagnetic materials have been prepared and investigated. The studies were often performed on thin films obtained either by thermal evaporation onto a cold substrate [1, 2] or by splat cooling [3, 4, 5]. Some studies were also performed on bulk materials [6].

For our work, amorphous magnetic Fe-Ge alloys have been studied in which the magnetic iron atoms are supposed to be randomly distributed in an amor-

phous diamagnetic matrix of germanium atoms. The interest of such amorphous medium is that enables one to vary the concentration of magnetic impurities in a very large range. Thus we can go from an amorphous semi-conductor alloy for low Fe concentrations to an amorphous metallic magnetic alloy for upper Fe concentrations.

2. Experimental results. — The amorphous alloys of Fe-Ge have been prepared in thin film form by

thermal evaporation (R. F. heating or electron bombardment) under high vacuum from a molten Fe-Ge ingot. The vapor was condensed on a glass substrate cooled at 77 K. The composition of the amorphous films was measured by X-ray fluorescence. Because of the difference between the vapor pressures of iron and germanium, the composition of films is quite different from that of the molten source. Up to 64 at. % of Fe, the Fe concentration in the film is significantly smaller than in the ingot (Fig. 1).

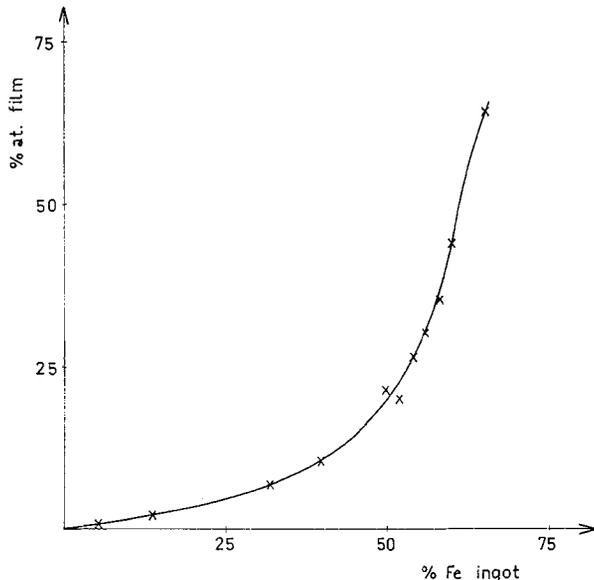


FIG. 1. — Composition of the films in function of the composition of the molten source.

3. Structure. — The composition of studied films ranged from pure Ge to 75 at. % of Fe. The structure of these films is analysed by electron diffraction. For all concentrations of iron we obtain the diffuse broad rings characteristic of amorphous materials. On increasing the Fe concentration the radius of the first broad ring is observed to increase gradually while its intensity gets smaller, it practically disappears above 20 at. % of Fe. The radius of the second ring somewhat decreases and its intensity increases.

The position of the different rings in function of iron concentration is represented on figure 2.

The radius of the first ring is given by the first maximum of the diffraction pair function

$$\frac{\sin 2 \pi s r_m}{2 \pi s r_m}$$

where s is the angle of diffraction and r_m the distance between the near neighbour diffracting objects on the amorphous material [7]. This first maximum is obtained for

$$S_m = \frac{2 \sin \theta_m}{\lambda} = \frac{1.23}{r_m}. \quad (1)$$

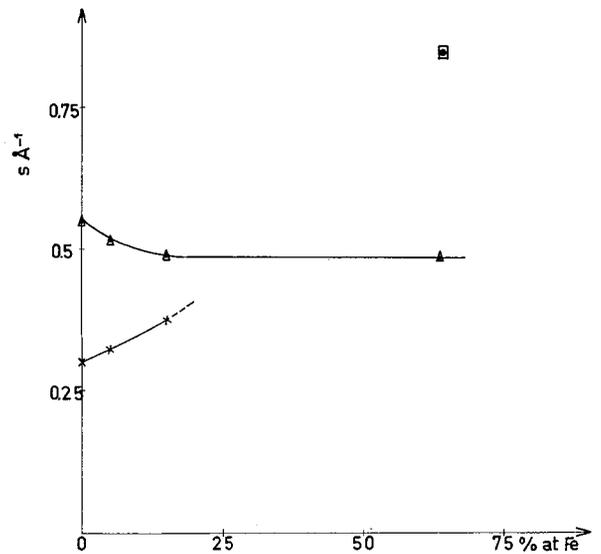


FIG. 2. — Variations of radii of broad rings of electron diffraction diagrams versus Fe concentration.

* First ring, Δ Second ring, \square Third ring.

In pure amorphous germanium the diffracting objects to consider are not the individual Ge atoms but the tetrahedra made of four Ge atoms. On introducing iron in the amorphous Ge, for low concentration of iron, the iron goes probably in substitutional positions as in crystalline Ge without disturbing very much the tetrahedra packing. This explains why up to 20 at. % Fe the diffuse ring system is not much changed. As Fe ratio increases the tetrahedra progressively breaks up and now the diffracting objects are the Fe and Ge atoms themselves. The minimum distance between them being smaller than the minimum distance between the tetrahedra, the radius of the first diffuse ring must increase.

In the amorphous alloy containing 64 at. % Fe, from the position of the first broad ring, we get from eq. (1) the distance between nearest neighbour diffracting objects :

$$s = 0.490 \text{ \AA}^{-1} \\ r = 2.5 \text{ \AA}.$$

This is very close to the distance separating Ge atoms and Fe atoms in their respective crystalline form :

$$d_{\text{Ge-Ge}} = \frac{a \sqrt{3}}{4} = 2.45 \text{ \AA} \quad a = 5.66 \text{ \AA}$$

$$d_{\text{Fe-Fe}} = \frac{b \sqrt{3}}{2} = 2.48 \text{ \AA} \quad b = 2.87 \text{ \AA}.$$

A second broad ring can be observed with the characteristic shoulder on it, which has been observed in amorphous materials [7]. Thus the diffraction results lead us to conclude that at high concentration of Fe, the Fe-Ge films are truly amorphous materials which can be considered as a dense packing of hard

spheres of same radii as the individual Ge and Fe atoms.

Recrystallisation of a 64 at. % Fe amorphous film has been performed in the electron microscope by locally heating by the electron beam.

The diffraction diagrams before and after crystallisation are given on figure 3. Beside the crystalline Fe ring system which is predominant, we can see a very faint barely visible 111 Ge ring and two faint rings of Fe₂Ge indexed as 110 and 002.

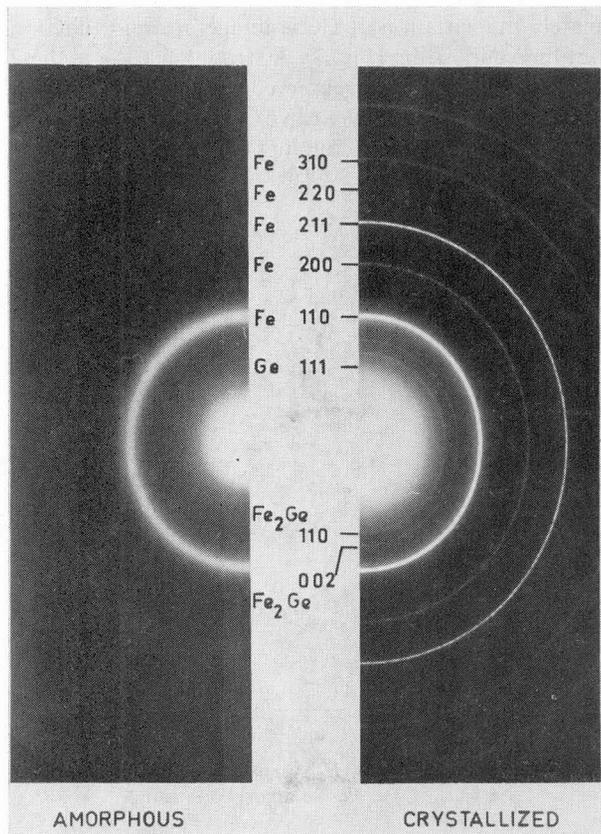


FIG. 3. — Electron diffraction diagrams of a 64 at. % Fe Fe-Ge alloy. Left amorphous structure, right recrystallized structure.

4. Electrical properties. — The electrical resistivity of Fe-Ge amorphous films for various concentrations of iron is shown on figure 4 while activation energies at 250 K and 100 K are given in table I. A Mott

TABLE I

Activation energies for different Fe concentrations

| Composition % at. Fe | 0 | 14 | 2 | 5 | 7 | 10 | 20 | 32 |
|----------------------|------|-------|-------|-------|-------|-------|----|----|
| E at 250 K ev | 0.14 | 0.13 | 0.08 | 0.07 | 0.045 | 0.017 | — | — |
| E at 77 K ev | 0.08 | 0.064 | 0.045 | 0.025 | 0.016 | 0.003 | — | — |

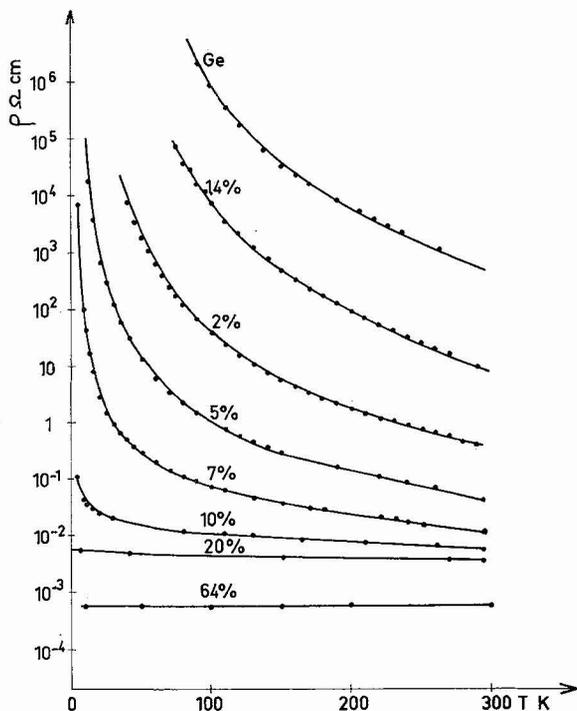


FIG. 4. — Resistivity of Fe-Ge alloys versus temperature for different Fe concentration.

$T^{-1/4}$ law is obeyed for concentrations in iron up to 25 at. % (Fig. 5). Above 25 % conduction is clearly metallic.

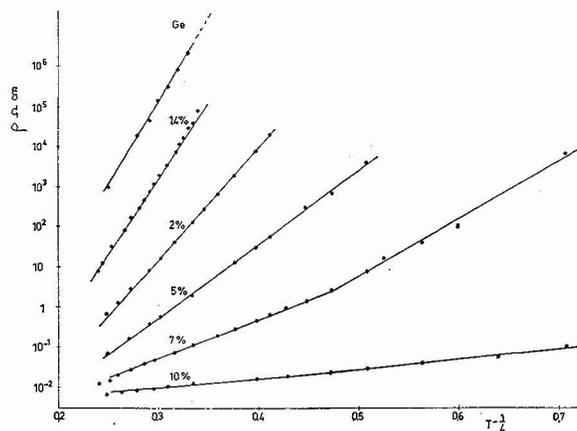


FIG. 5. — Resistivity of Fe-Ge alloys versus $T^{1/4}$ for different Fe concentration.

5. Magnetic properties. — Magnetic properties of these films have been investigated by magnetic resonance technique, hysteresis loop measurements and Lorentz electron microscopy. Above 25 at. % Fe a ferromagnetic resonance could be detected.

By measuring the position of the resonance line with the applied magnetic field either perpendicular

or parallel to the plane of the film, we can determine the spontaneous magnetization M_s through the formula

$$\left. \begin{aligned} H_{\text{res}} &= \frac{\omega}{\gamma} + 4\pi M_s && \text{for } H \perp \text{ film} \\ \frac{\omega}{\gamma} &= \sqrt{H_{\text{res}}(H_{\text{res}} + 4\pi M_s)} && \text{for } H // \text{ film} \end{aligned} \right\} \quad (2)$$

Measurements have been performed at 300 K and 77 K for several concentrations of iron and the values of spontaneous magnetization obtained from eq. 2 are reported on figure 6. This shows that long range magnetic ordering occurs for Fe concentrations upper than 25 at. %. If we assume that exchange interaction extends only to near neighbour Fe atoms, a simple

percolation argument tells us that for Z the number of near neighbour around each atom, and assuming a random distribution of Fe and Ge atoms, the critical concentration of magnetic ions C_t for ferromagnetism onset has the value : $C_t \sim 2/Z$.

Taking C_t equal to 25 % gives us a coordination number Z of the order of 8 for this range of Fe concentrations. This is not unrealistic since with pure Ge or with low Fe content, Z is the order of 4 (tetrahedra structure) while with high Fe concentration, the hard spheres model predicts $Z \simeq 12$.

From the results of figure 6, we can draw approximately the variation of Curie temperature in function of film composition (Fig. 7). A striking feature in these alloys is the absence of observed resonance absorption in paramagnetic state. We can explain that by assuming that strong spin-orbit coupling of Fe^{2+} as well as a

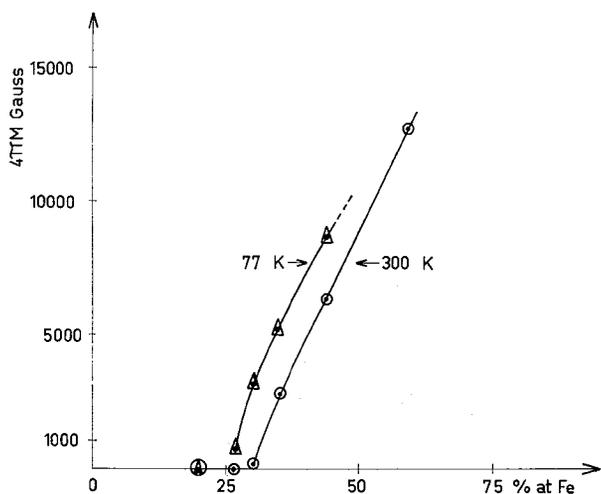


FIG. 6. — Spontaneous magnetization versus Fe concentration.

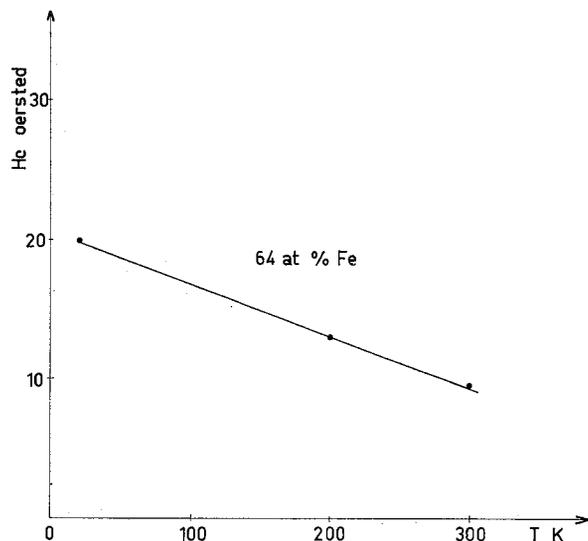


FIG. 8. — Coercive force H_c versus of temperature for a 64 at. % Fe, Fe-Ge amorphous alloy.

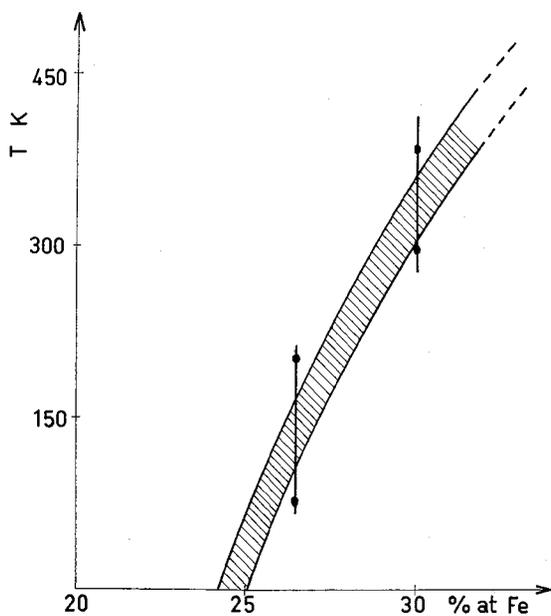


FIG. 7. — Variation of the Curie temperature versus Fe concentration.

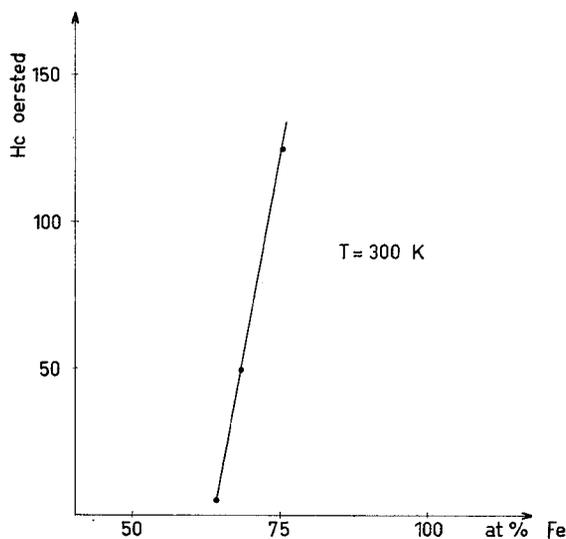


FIG. 9. — Coercive force H_c versus films composition.

random static crystal field due to the amorphous nature of the matrix may make difficult the observation of the signal. It has also been suggested by Mott (*) that superexchange antiferromagnetic interaction between iron atoms in a narrow band is to be expected and which will contribute to enhanced spin-relaxation. So it will be interesting to investigate more thoroughly the behaviour of resonance absorption as a function of temperature. Hysteresis loops have been also

investigated for three different Fe concentrations at room temperature. Measurements were made by means of Kerr effect apparatus and vibrating magnetometer.

The hysteresis loops are square, implying uniform magnetization in the film.

Measurements made on a 64 at. % Fe film show a nearly linear decreasing of the coercive force H_c in function of temperature. But the value of H_c is always small, $H_c < 20$ Oe (Fig. 8).



PHOTO 1.

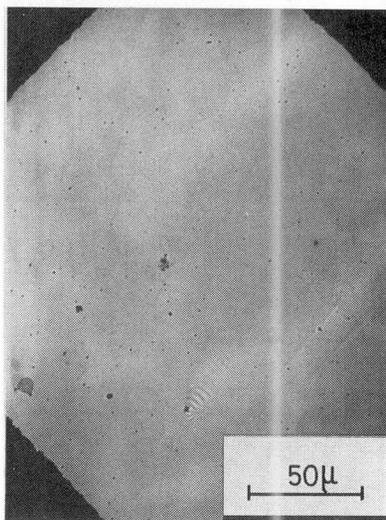


PHOTO 2.

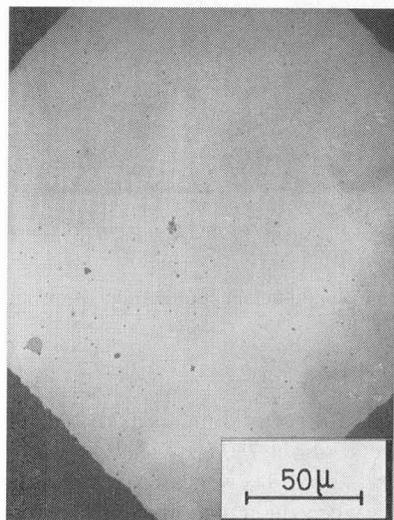


PHOTO 3.

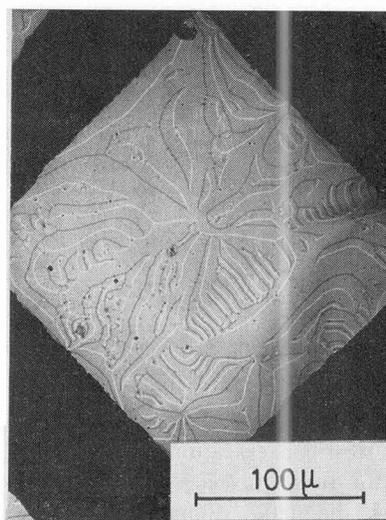


PHOTO 4.

FIG. 10. — Lorentz micrographs of a 34 at. % Fe Fe-Ge amorphous alloy.

(*) Private communication.

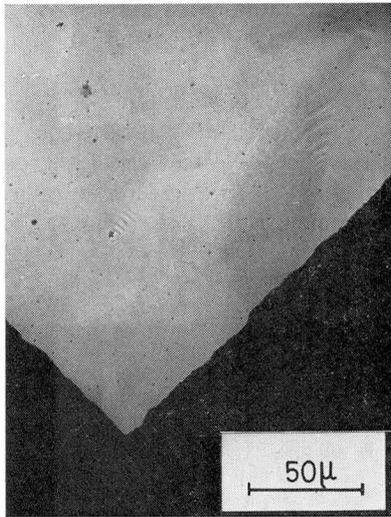


PHOTO 1.

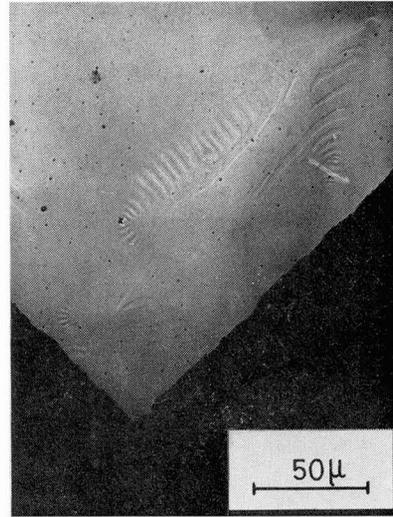


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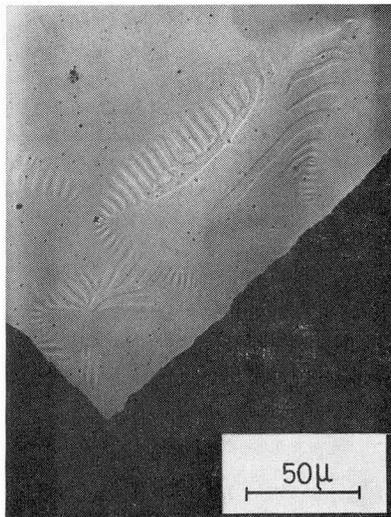


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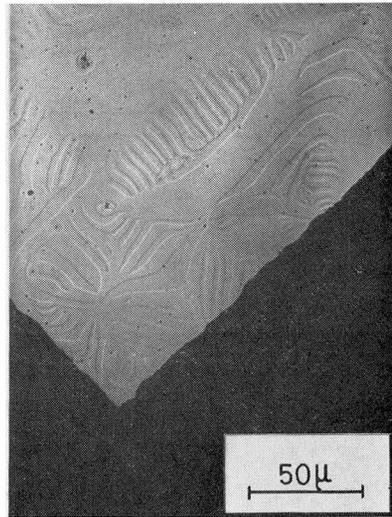


PHOTO 4.

FIG. 11. — Lorentz micrographs of the same sample for different decreasing temperatures.

On figure 9 we have drawn the variation of H_c in function of the iron concentration at $T = 300$ K. This variation is also quasi linear.

Observations of magnetic domains have been performed by means of Lorentz electron microscopy technique. These observations have been made on a film containing 34 at. % Fe. At room temperature this alloy has a spontaneous magnetization

$$4\pi M_s = 1\,600\text{ G}$$

measured by ferromagnetic resonance, but at this

temperature any domain is visible. The domains take place at about 280 K (Fig. 10).

On figure 11 we can see how the domains take place when the temperature is progressively decreased.

Recrystallization of this film has been performed in the electron microscope by locally heating by means of the electron beam. Figure 12 shows the recrystallized area where the domain structure is destroyed. From these Lorentz micrographs we can say that at room temperature the magnetization is too weak and perhaps out of the plane of the film.

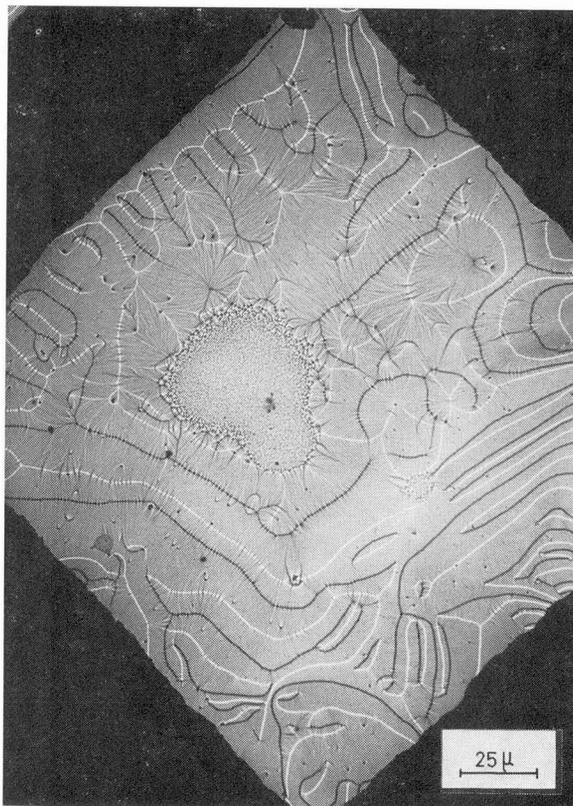


FIG. 12. — Lorentz micrographs of the 34 at. % Fe Fe-Ge amorphous alloy, at 77 K and with a recrystallized area.

6. Conclusion — These Fe-Ge amorphous alloys are an extremely interesting example of an amorphous medium whose short range ordering changes progressively on increasing the Fe concentration. It is also remarkable that the critical percolation concentration for the onset of ferromagnetism coincides

with the onset of metallic conductivity. It will be quite interesting to investigate other physical properties like susceptibility in paramagnetic state to find out if spin-glass transition is observed or not in such a system.

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