

Structural resonances in amorphous CdGeAs₂-Fe alloys

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(Submitted 24 October 1990; resubmitted 6 December 1990)

Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 1, 42–45 (10 January 1991)

The behavior of Fe in glassy CdGeAs₂ has been studied. A new effect, consisting of “structural resonances,” has been observed. These resonances are abrupt, nonmonotonic changes in the structure and physical properties of amorphous alloys, including huge changes (by a factor of 1.5–2) in the density of the substance at critical values of the Fe concentration.

The cluster structure of amorphous semiconductors, which arises from a self-organization of the structure under the influence of chemical-binding forces, determines the stability of materials of this class with respect to external agents and has a decisive effect on the effectiveness of a doping.¹⁻⁴ The features of cluster conversions in materials of various compositions which we have studied suggest that structural phase transitions of the nature of “resonances”—substantial reactions of the system to small changes in composition—can occur, in addition to the formation of dopant clusters,^{1,4} when amorphous substances are doped. The nature of the structural resonances is

associated with the possible appearance of equilibrium or metastable compounds of stoichiometric composition instead of heterophase structures when the concentrations of the components of the amorphous alloy satisfy certain critical relations. These concentrations can probably be predicted on the basis of the positions of singular points on the corresponding state diagrams, if the latter exist.

We have observed resonances of this sort in a study of the effect of the Fe concentration on the structure, density, electrical conductivity, and x-ray emission spectra of $(\text{CdGeAs}_2)_{100-x}\text{Fe}_x$ amorphous films. Films 2–7 μm thick were synthesized through a cosputtering of targets in an argon atmosphere.⁵

Two diffuse maxima or halos, I and II, are seen against a background on the x-ray diffraction patterns of the films. The peaks stem primarily from a coherent scattering of x radiation by clusters of two types, with a crystal-like packing of atoms.¹ The background, which intensifies with increasing diffraction angle, arises because of an incoherent scattering of the radiation by the medium with disordered atoms between clusters (Fig. 1). The structure of the films undergoes substantial changes with in-

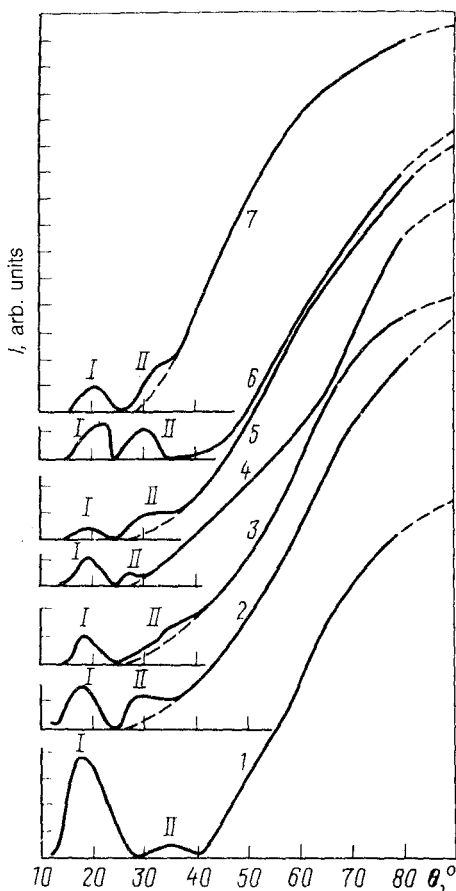


FIG. 1. Diffraction patterns of $(\text{CdGeAs}_2)_{100-x}\text{Fe}_x$ films in Fe radiation. x , %: 1—0; 2—9.4; 3—15.0; 4—38.8; 5—39.2; 6—40.3; 7—42.1.

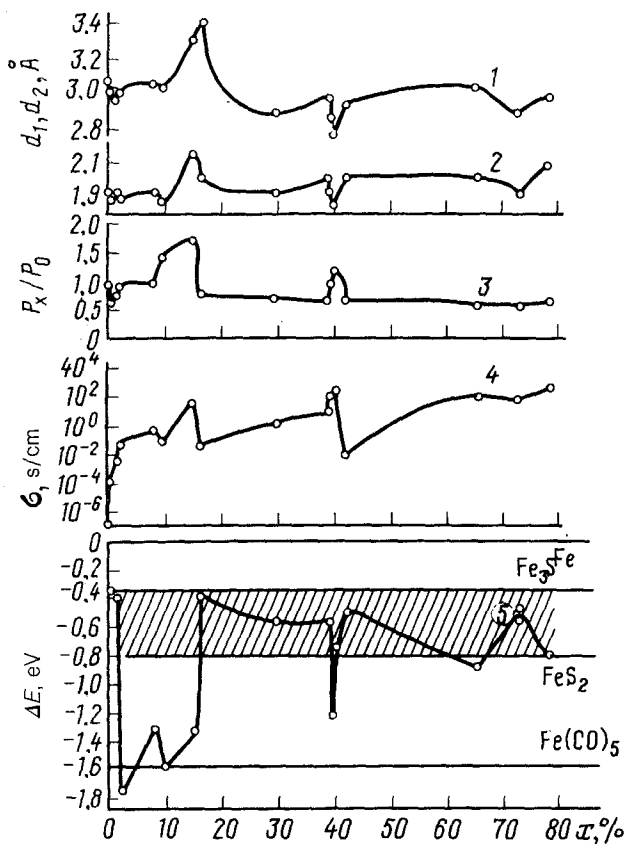


FIG. 2. Parameters of the sample versus the Fe concentration. Here P_0 is the density of the undoped films.

creasing Fe concentration. As can be seen from Fig. 1, changes occur in the shape, position, and integral intensities I_1 and I_2 of the halos. The curves of $I_1(x)$ and $I_2(x)$ are not monotonic. At $x = 0$ we find a ratio $I_2/I_1 \approx 0.05$; this ratio increases by several orders of magnitude in alloys containing Fe. The curves of the mean interplanar distances in the clusters, $d(x)$ (curves 1 and 2 in Fig. 2), calculated from the positions of the halos on the Debye patterns, also indicate substantial structural changes in the films. Measurements of the density and electrical conductivity of the films (at $T = 300$ K; curves 3 and 4) yield results in good agreement with the structural changes.

Of primary interest in Fig. 2 are the following Fe concentration intervals: $0 < x < 5$ (0–0.9% Fe by weight), $8 < x < 17$ (1.4–3.2% Fe by weight), and $39 < x < 42$ (9.6–10.8% Fe by weight). In these intervals, the substantial changes stimulated in all the parameters of the samples by slight changes in the Fe concentration stem from radical changes in the nature of the interatomic interactions. Direct confirmation of this assertion comes from the results of a study of the Fe $K\beta_1$ x-ray emission spectra. The Fe $K\beta_1$ line is a triplet⁶⁻⁸ Fe $K\beta'_1\beta_1^5\beta_1^7$. The energy position of β'_1 with respect to β_1^7 is determined by the $3p-3d$ Coulomb interaction, and that of β_1^5 is determined by

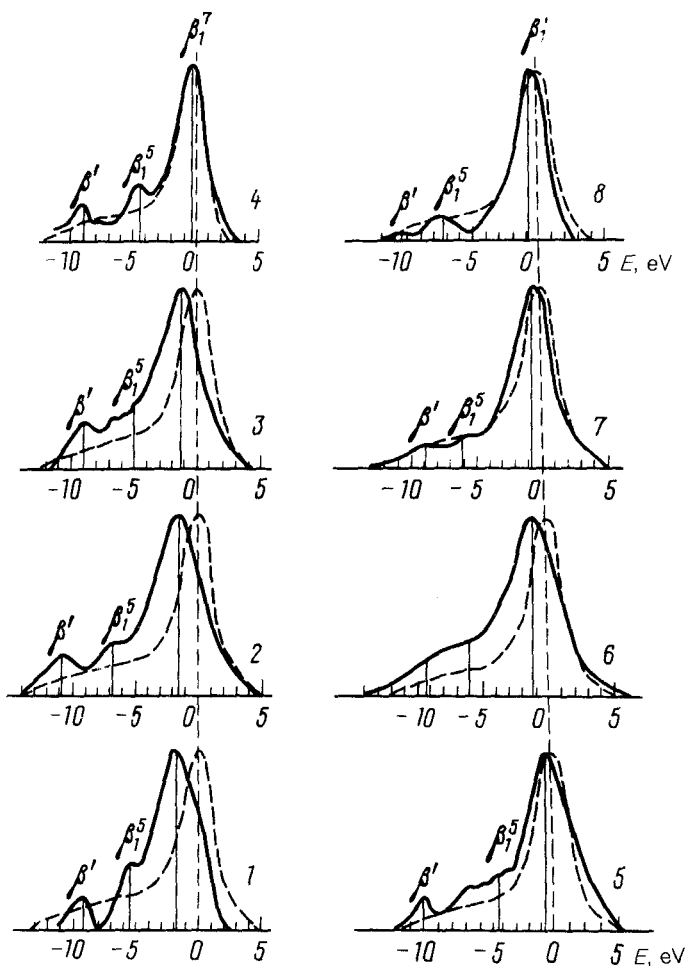


FIG. 3. Some x-ray emission spectra of the films. x , %: 1—8.1; 2—9.4; 3—15.0; 4—16.5; 5—38.8; 6—39.2; 7—40.3; 8—42.1. Dashed curves—Spectra of metallic Fe.

the $3d-3d$ Coulomb interaction. The spatial localization of the low- and high-energy groups of electrons is manifested in an isolation of the corresponding multiplets, β_1^5 and β' . As the exchange interactions strengthen during the formation of covalent bonds of Fe atoms with host atoms, the isolation of multiplet β_1^5 , at $x = 15$, or the multiplets β' and β_1^5 , at $x = 39-40$, weakens near critical concentrations. Changes in the nature of the interaction of the Fe atoms with the host atoms can also be seen clearly from a shift of the β_1^7 line with respect to its position in a sample of metallic iron, as shown by the dashed curves in Fig. 3. In all cases, the line shifts in the long-wavelength direction, indicating a lowering of the energy of the valence band upon the transition from a metal to a compound, as a result of a sharp strengthening of the exchange interaction due to a localization of valence electrons in certain preferred directions.⁸ The magnitude of the shift, ΔE , which is determined by the binding energy

of the Fe atoms with their nearest neighborhood, at times increases sharply to $- (1.25-1.75)$ eV during structural resonances and at times returns to the region of the most common values, $\Delta E = - (0.4-0.8)$ eV (curve 5 in Fig. 2). Values $\Delta E = - (0.4-0.8)$ eV correspond to compounds with covalent bonds, of the type Fe_3S , Fe_3Si , and FeS_2 , with an ordering of atoms in corresponding planes.^{6,9} Very large long-wavelength shifts, on the order of $- 1.5$ eV, of the line $\text{Fe } K\beta_1^7$ are characteristic of more-complex compounds with covalent binding such as iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, with an ordered arrangement of CO groups in the form of a trigonal bipyramid around Fe atoms.⁹

The substantial changes in the shape of the Fe $K\beta_1$ line, the significant energy shifts of this line, and the huge changes in the density (by a factor of 1.5–2), d_1 and d_2 (from 8% to 18%), and the electrical conductivity (by three to five orders of magnitude) are evidence of the formation of new structural states of the substance at Fe concentrations corresponding to structural resonances. These new states, with a more refined structure [as can be seen from the peaks in the intensities of the coherent scattering, $I_2(x)$ and $I_2(x)$], a ultradense packing of atoms, and a high electrical conductivity—a consequence of a restructuring of the electron spectrum—exist in narrow intervals of the Fe concentration. We do not rule out the possibility that a bulk ordering of atoms of the original substance around Fe atoms occurs in the course of the structural resonances, as it does, for example, in $\text{Fe}(\text{CO})_5$.

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Translated by D. Parsons