Phase transition from the amorphous to the polycrystalline state in ferromagnetic Co-P films

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The spin-wave resonance method ($f = 9.2$ GHz) was used to investigate the phase transitions from the amorphous to the crystalline state and from the hexagonal to the cubic structure in magnetic cobalt-phosphor films (9 at. % P). The temperature dependence of the exchange-interaction constant $A(T)$ was measured in the interval 300–700 °K in the presence of the indicated transitions.

The investigated objects were three-layer films obtained by chemical precipitation.[1] The thickness of the main (central) layer was 1000—3000 Å. Additional layers 200—300 Å thick, the magnetization of which was respectively larger and smaller than the magnetization of the main layer, served to produce special boundary conditions (in this case, antisymmetrical pinning). The use of such boundary conditions makes it possible to eliminate the possible influence of the change of the surface pinning during the heating of the sample on the result of the measurements of the exchange constant.[3] We observed in the spin-wave resonance (SWR) spectrum of the investigated films 9—11 modes, with a quality factor $H_p/\Delta H \sim 80$. The quadratic dependence of the resonance field of the mode on its number makes it possible to use the Kittel dispersion relation to determine the exchange constant. The resonance fields of the modes and the exchange constant were measured with accuracy ± 0.2% and ± 5%, respectively.

Figure 1 (curve 1) shows the dependence of the exchange constant on the temperature. The $A(T)$ curve is characterized by two discontinuities: the first is a sharp drop of the exchange constant at 530 °K, followed by a slow variation, and the second is a sharp rise at 640 °K. The resonance field of the fundamental mode of the spectrum varies in similar fashion.

The electron-diffraction and x-ray diffraction patterns of the obtained precipitates in the initial state are characterized by smeared diffraction maxima, thus proving that they are amorphous (Fig. 2a). The amorphous character of the Co—P films is confirmed also by analysis of their thermograms, which are characterized by the presence of an exothermal peak at 530 °K, corresponding to a transition from a nonequilibrium (amorphous) state to an equilibrium state.[2]

X-ray diffraction patterns of these samples were taken at temperatures 293—750 °K (Fig. 2). In the temperature range 510—550 °K there appear clear-cut reflections that characterize the hexagonal cobalt (α phase). The x-ray diffraction pattern characterizing the start of the transition to the crystalline state (α-Co) is shown in Fig. 2b. At 640—690 °K, the x-ray diffraction patterns show evidence of a transition of the α phase into the β phase. Figure 2c shows an x-ray diffraction pattern obtained at 680 °K. The peak with the higher in-

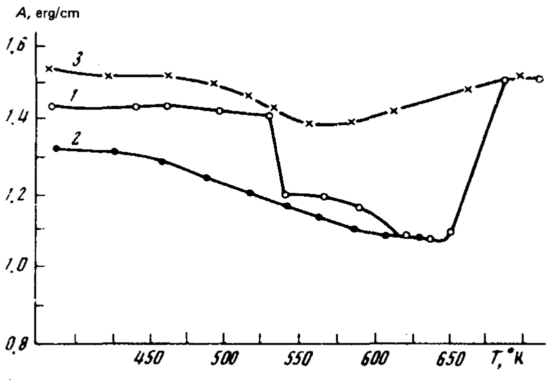

FIG. 1. Temperature dependence of the exchange-interaction constant of a Co—P film: 1) plot of $A(T)$ of amorphous sample; 2) $A(T)$ after annealing at 570 °K; 3) $A(T)$ after annealing at 690 °K.

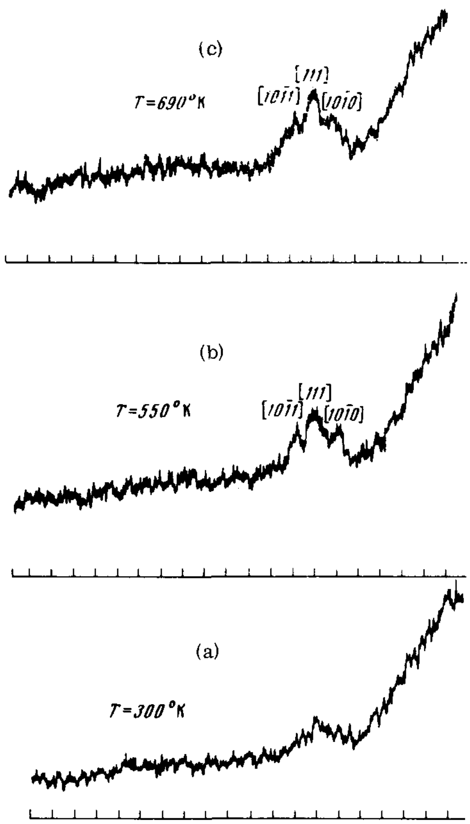

FIG. 2. a—x-ray diffraction pattern of amorphous Co—P film (9 at. % P); b—x-ray diffraction pattern obtained in the initial stage of crystallization, the reflections 1010 and 1011 characterize the hexagonal phase and 111 the cubic phase of cobalt; c—x-ray diffraction pattern obtained in the final state of the polymorphic α-Co—β-Co transition.

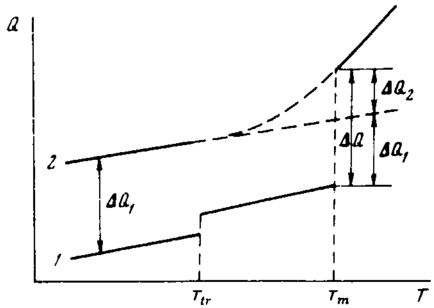

FIG. 3.

tensity in this pattern corresponds to the cubic phase of cobalt (β-Co). The thermograms of the Co—P films have two maxima characterizing the exothermal reaction, one in the temperature region 510—550°K and the other at 640—690°K.

The variation of the exchange-interaction constant during the course of cooling of the samples from 570 and 690°K is shown by curves 2 and 3 respectively in Fig. 1. During the subsequent cycles of heating and cooling of the samples in the indicated temperature intervals, the exchange-interaction constant values were reproducible within the limits of the measurement error, and agreed with the indicated curves.

Let us see the extent to which the obtained temperature dependence of the exchange constant $A(T)$ and the thermogram of the Co—P films are "compatible" with the change of the heat content $Q = \int C_p\, dT$ with changing temperature, for both the crystalline and the amorphous modifications. As is well known, the polymorphic transformations of α-Co into β-Co proceed with a small change of heat content. The reason is that α-Co and β-Co are characterized by identical coordination numbers. When the heat contant of the crystal (curve 1) is compared with that of the amorphous substance (curve 2), the initial reference can be the $Q = f(T)$ curve above the melting temperature T_m.[4] The quantity ΔQ (Fig. 3) is the latent heat of melting of the crystal ($\Delta Q = 58.2$ cal/g for cobalt). Part of this heat (ΔQ_1) goes to destroy the long-range crystallographic order and the rest (ΔQ_2) to rearrange of the short-range order to fit the structure of the liquid at T_m. Usually ΔQ_1 and ΔQ_2 are of the same order. On going from the melt to the amorphous form, only ΔQ_2 is released, and the quantity ΔQ_1 is a measure of the disorder of the amorphous substance.

We consider the following explanation of the results to be the most probable: The Co—P film was obtained in a nonequilibrium state (curve 2, Fig. 3). A measure of the deviation from equilibrium is the quantity ΔQ_1. Heating in the temperature region near 530°K produces an irreversible transition to the crystalline modification (α-Co). This is accompanied by a release of ΔQ (a large peak on the thermogram). Further heating produces a polymorphic α-Co → β-Co transition accompanied by absorption of a small amount of heat ($\Delta Q' = 1.05$ cal/g). At this temperature the thermogram shows a small heat-release peak. Additional investigations have shown that precipitation of Co_2P, accompanied by release of heat,[2] occurs in the region 640—680°K. This is in all probability reflected in the thermogram.

Thus, curve 3 of Fig. 1 characterizes a crystalline α-Co film, curve 1 of Fig. 1 corresponds to the amorphous phase of the Co—P film, the short-range order of which is analogous to β-Co (Fig. 3, curve 2), while the film in the hexagonal phase corresponds to curve 2 of Fig. 1.

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