MAGNETIC, MAGNETO-OPTICAL, AND TRANSPORT PROPERTIES OF ORDERED AND DISORDERED 3d-TRANSITION METAL ALUMINIDE FILMS

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ABSTRACT

The influence of the order-disorder structural transition on the magnetic and magneto-optical, and transport properties of Fe-Al and Co-Al alloy films has been investigated. The disordered states in the alloy films were prepared by vapor quenching deposition on glass substrates cooled by liquid nitrogen. The experimental study of the magneto-optical properties of the ordered and disordered Fe-Al and Co-Al alloy films has been carried out in 1.05 - 5.0 eV energy range at room temperature. The transport properties have been measured in 2 - 300 K temperature range with and without magnetic field of 0.5 T. The influence of the order-disorder structural transition on the magnetic and magneto-optical properties was discussed by using the effective medium approximation and the structural defect approach. That on the temperature dependence of the resistivity was analyzed in a framework of the partial localization of the electronic states and the variable range hopping conductivity.

1. INTRODUCTION

In the perfectly ordered stoichiometric FeAl or CoAl compound, Fe or Co and Al atoms form interpenetrating primitive cubic lattices, where each Fe or Co atom has 8 Al atoms as the nearest neighbor and *vice versa*. There is a general consensus that these compounds are not magnetic even at very low temperatures, even though the ground state of FeAl is still open to question [1-4]. The minima of the paramagnetic and ferromagnetic total energies of FeAl are very close to each other : the equilibrium lattice constants for two states differ by about 0.1% and the ferromagnetic energy minimum is lower by only 0.7 mRy. Hence a formation of magnetic clusters in this system seems plausible.

A slight atomic disorder leads to the occurrence of local magnetic moments. It is widely believed that these moments are induced from so-called antistructure Fe or Co atoms (Fe-ASA or Co-ASA) - Fe or Co atoms at Al sites. Indeed, the appearance of 1 Fe-ASA or Co-ASA leads to a formation of 9-atom Fe or Co cluster, which can carry a magnetic moment. Taking into account the similarity between the physical properties of 3d-TM aluminides and gallides [5,6], it can be supposed that the ferromagnetic behavior of the Fe-Al and Co-Al alloys arises essentially from interactions between, at least, a couple of ASA.

In contrast to the ordered state of Fe-Al or Co-Al alloy, in the disordered state Fe or Co and Al atoms randomly occupy the sites of bcc lattice. This change in the symmetry and basis of the unit cell itself should lead to drastical changes in the electronic energy structures (EES). Moreover, an increase in the lattice parameter of the disordered state is often connected with an increase in the atomic radius of Al, caused by a charge transfer in opposite direction - from Fe or Co to Al [7]. Therefore, it can be expected that order-disorder transformation in the nearly equiatomic FeAl alloys and the Co-rich β-phase Co-Al alloys leads to the changes in their EES and physical properties.

In this paper we study experimentally the influence of the structural order-disorder transition in nearly equiatomic FeAl alloy film and Co-rich β-phase Co-Al alloy film on their

magnetic, magneto-optical (MO) and transport properties and analyze the obtained data in terms of formation of defect structures as well as lack of translational invariance.

2. EXPERIMENT

For thin film preparation the homogeneous alloy ingot was crushed into powders of 80 - 100 µm in diameter. Alloy films with a total thickness of 100 - 150 nm have been prepared onto glass substrates in a high vacuum of 5 x 10^{-5} Pa by flash evaporation. The deposition rate was about 2 nm/s. Such a high deposition rate allows to reduce the volume contamination and oxidation. An equilibrium ordered state was obtained by the deposition onto substrates heated up to 680 - 720 K. To obtain the disordered state a vapor quenching deposition was employed, where a chaos of gas phase is condensed onto glass substrates cooled by liquid nitrogen. The substrate temperature during the deposition was about 150 K.

The structural analysis of the films has been performed by using transmission electron microscopy (TEM) of the films of 60 - 100 nm thickness, obtained at the similar conditions onto fresh chips of single-crystalline NaCl. The x-ray fluorescence analysis for the elemental contents of the prepared films revealed 52 at.% of Fe and 48 at.% of Al, and 62 at.% of Co and 38 at.% of Al.

The field dependence of the magnetization for the ordered and disordered alloy films was measured using a vibrating sample magnetometer (VSM) at room temperature (RT) in a magnetic field up to 1.8 T for an in-plane geometry. The ferromagnetic resonance (FMR) of the films was studied at 9.3 GHz and RT in a parallel configuration. The resistance measurements were carried out by using the four probe technique in a temperature range of 2 - 300 K with and without an external magnetic field of 0.5 T, directed in the film plane.

MO properties (eqatorial Kerr effect : EKE) of the ordered and disordered alloy films were investigated at RT by the dynamical method using p-plane polarized light at two angles of incidence (66 and 75 degrees) in a spectral range of 250 - 1100 nm (5.0 - 1.05 eV) and in an AC saturation magnetic field. The EKE value, $\delta = \Delta I/I_0$, is the relative change in the intensity of reflected light, caused by the magnetization of the sample in an external magnetic field directed transversely to the plane of the light incidence.

3. RESULTS AND DISCUSSION

According to the results of TEM study on the $Fe_{0.52}Al_{0.48}$ alloy film, the film deposition on glass substrates at 680 K leads to the formation of the ordered alloy structure with a mean grain size of about 30 nm. A series of superstructure rings, which are attributed to the reflection from (100), (111) and (210) atomic planes, are clearly seen. This result shows that a stable phase of superlattice, expected from the equilibrium phase diagram for bulk FeAl system, is formed under our deposition conditions. A decrease in the substrate temperature to 150 K leads to the formation of a considerably disoredered polycrystalline film (a few smeared diffraction rings are seen) with a mean grain size of 10 - 15 nm. Similar results were obtained for the prepared $Co_{0.62}Al_{0.38}$ alloy films.

The in-plane magnetization loop, M(H), of the ordered $Fe_{0.52}Al_{0.48}$ alloy film exhibits two regions - an increase in the magnetic moment with an applied magnetic field up to 1500 Oe, followed by a gradual decrease (see Fig. 1). Such a behavior can be produced by a mixture of ferromagnetic and nonmagnetic phases, which means that the ordered films are not homogeneous in magnetic and hence atomic senses. It can be supposed that in these samples there are some ferromagnetically coupled Fe-ASA or their clusters embedded into a nonmagnetic FeAl alloy matrix.

The transition of the $Fe_{0.52}Al_{0.48}$ films from an ordered state into disordered one causes a significant growth of the magnetic moment ; the field dependence of M also changes. It is seen that M(H) curve for the disordered state exhibits two different parts : a rapid growth of

the magnetization in a comparatively low (up to about 200 Oe) magnetic field, and a gradual increase in the effective magnetic moment with a field up to 8000 Oe. It indicates that the disordered state is not homogeneous either in magnetic sense : there are both soft magnetic phases and other phases in which an external magnetic field induces magnetic moments. In other words, it can be supposed that such a behavior is caused by the existence of the different atomic arrangements of the Fe-ASA.

The M(H) loops of both ordered and disordered $Co_{0.62}Al_{0.38}$ alloy films exhibit nearly the same field dependence. The transition of the $Co_{0.62}Al_{0.38}$ alloy films from the ordered state into disordered one causes an increase in the magnetic moment by about 20% and an increase in the coercivity from 110 to 260 Oe. As far as the magnetic moments in Co-Al alloys result from the Co-ASA (Co clusters), such a behavior of M(H) indicates that the structural disordering forms more Co-ASA

Fig. 1. Magnetization loops of $Fe_{0.52}Al_{0.48}$ films. "1" and "2" for the ordered and disordered states, respectively.

than in the ordered state. The obtained FMR spectra of the $Fe_{0.52}Al_{0.48}$ and $Co_{0.62}Al_{0.38}$ films are correlated qualitatively with the respective magnetization data by VSM.

The experimental EKE spectra of the ordered and disordered $Fe_{0.52}Al_{0.48}$ films are shown in Fig. 2, together with the results of computer simulation. It is seen that the EKE spectrum of the ordered alloy film shows a very low intensity and no prominent feature in the investigated spectral range. The transition into the disordered state causes a drastic growth in the EKE value and a change in the shape of the spectrum.

In order to deduce the possible reasons for the changes the computer simulation of the EKE spectra were carried out. In this simulation it was supposed that $Fe_{0.52}Al_{0.48}$ alloy is represented by the ordered FeAl alloy with the Fe-ASA of a certain volume fraction. Then, the effective medium approximation (EMA) was employed. It was supposed that the MO response of $Fe_{0.52}Al_{0.48}$ alloy originates from the Fe-ASA or their clusters. It is reasonable to employ the optical and MO parameters of bulk Fe as a first approximation for the corresponding properties of Fe-ASA [8].

It is seen in Fig. 2 that the experimental EKE spectrum of the ordered $Fe_{0.52}Al_{0.48}$ alloy film reveals a significantly lower intensity than the simulation for an equilibrium concentration of the Fe-ASA of 0.02 (x = 0.02). The investigated ordered $Fe_{0.52}Al_{0.48}$ alloy films have a mean grain size of about 30 nm. If the width of the grain boundaries is assumed to be 0.5 nm, a simple calculation reveals that about 10% of the film volume are involved in the grain boundaries. It is well known that grain boundaries are usually in a highly disordered or even amorphous phase which may have significantly different MO properties from those of the ordered phase. Nevertheless, this is not enough to explain the disagreement between the experimental and simulated EKE spectra. Therefore, such a behavior of the experimental EKE spectrum indicates that the Fe-ASA in FeAl alloy matrix have considerably different properties from the bulk Fe atoms.

The transition of the $Fe_{0.52}Al_{0.48}$ alloy into a disordered state causes a drastic growth in the EKE value, and an apparent change in the sprectrum shape. The experimental values exceed
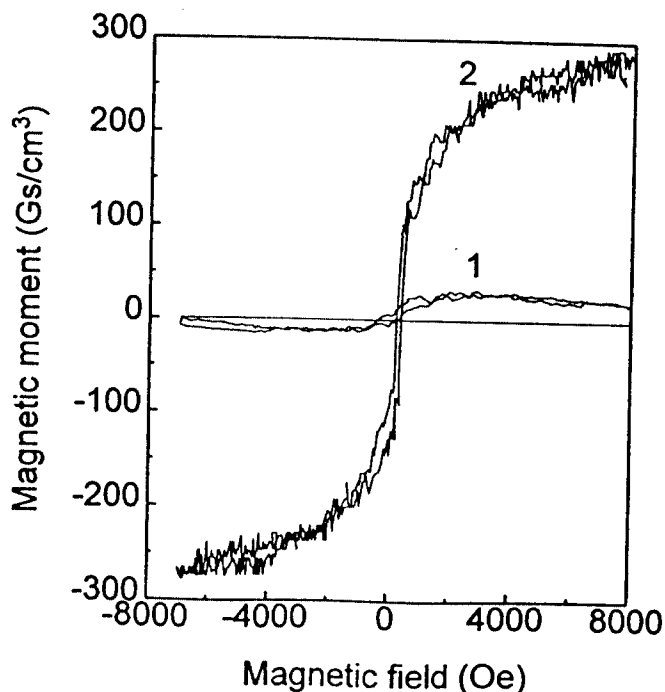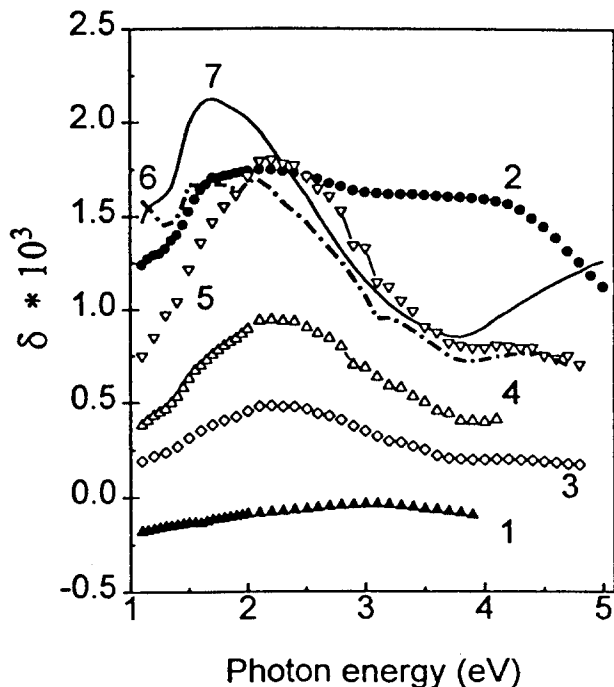
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Fig. 2. Experimental EKE spectra of $Fe_{0.52}Al_{0.48}$ films and a pure Fe film. "1" and "2" for the ordered and disordered alloy films, respectively. "7" for the pure Fe film for comparison, whose intensity is reduced 5 times. "3" - "6" for the simulated EKE spectra of the ordered FeAl with the Fe-ASA of volume fraction of x : "3," "4," "5" and "6" for x = 0.02, 0.04, 0.08 and 0.10, respectively.
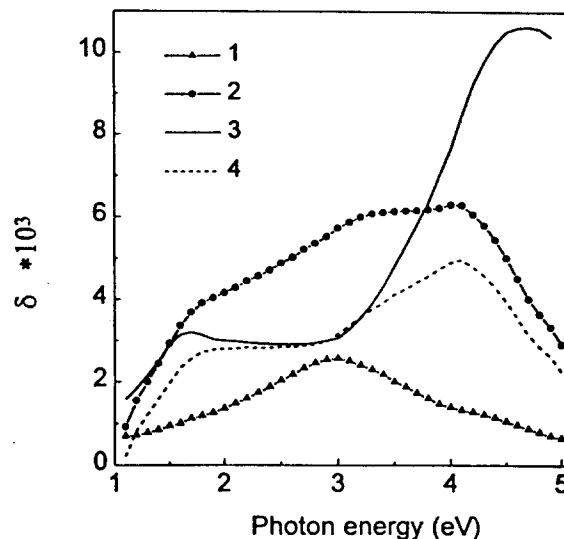
Fig. 3. Experimental EKE spectra of the $Co_{0.62}Al_{0.38}$ alloy films and a pure Co film at an angle of incidence of 66 degrees. "1" and "2" for the ordered and disordered alloy films, respectively. "3" for a pure Co film for comparison. "4" is the subtraction of the spectrum of the ordered $Co_{0.62}Al_{0.38}$ film from that of the disordered film.

significantly the simulation ones of the EKE spectrum for x = 0.04 which can be produced in bulk FeAl alloys by a high temperature quenching. A more reasonable agreement between the experimental and modelled EKE spectra is achieved when x = 0.08 - 0.10 is assumed, even though the apparent discrepancies in the shape are still exist. Therefore, it is concluded that even at 8 - 10% Fe-ASA the MO properties of the Fe-ASA or their clusters are significantly different from those of bulk pure Fe. Here it should be noted that the lattice parameter of the Fe clusters in the alloy is a = 2.908 Å, while a = 2.89 Å for pure Fe.

The experimental EKE spectra of the ordered and disordered $Co_{0.62}Al_{0.38}$ alloy films are shown in Fig. 3, together with the result for a pure Co film. The EKE spectrum for the ordered alloy films exhibits a prominent peak near 3 eV. A lack of the translational symmetry in the disordered state leads to a significant (at least, twice at 3 eV) growth of the EKE value and an apparent change in the shape of the spectrum. In the EKE spectrum of the disordered alloy films two maxima at 1.75 and 4.1 eV are clearly seen, and a feature near 3 eV also exists. The comparison of the latter spectrum with the EKE spectrum of pure Co reveals a similarity between them. The similarity becomes more obvious with the spectrum obtained by the subtraction of the EKE spectrum of the ordered $Co_{0.62}Al_{0.38}$ alloy films from that of the disordered one (see Fig. 3). Since the MO response originates from the Co-ASA, it can be supposed that in the disordered state there are a group of Co atoms whose MO properties are close to those of pure hcp Co. It was already mentioned that the only bcc and

B2 structures were detected in the TEM diffraction patterns. Therefore, this result can be interpreted by that the bcc Co atoms have very similar MO properties to usual hcp Co atoms. This also allows us to suppose some similarities in the EES between bcc and hcp Co atoms. A self-consistent density functional band-structure calculation for a hypothetical bcc Co has been performed by Bagayoko et al. [9], showing that there is little difference in EES between bcc and fcc Co, and hence between bcc and hcp Co.

The temperature dependence of the resistance of the ordered and disordered $Co_{0.62}Al_{0.38}$ alloy films normalized with respect to the resistance at RT is presented in Fig. 4. The following regularities are observed: i) all the $Co_{0.62}Al_{0.38}$ alloy films exhibits a prominent resistance minimum (T_{min}) in low temperature region; ii) the temperature dependence of the normalized resistance for alloy films in the ordered state shows a convex curvature in a region of 50 - 300 K, while for the disordered state a concave curvature is typical; and iii) the structural disorder shifts T_{min} to a higher temperature. The influence of the magnetic field on the resistance of the disordered $Co_{0.62}Al_{0.38}$ alloy films is illustrated in Fig. 4 (c). It is seen unexpectedly that T_{min} is not lowered in the presence of the external magnetic field. T_{min} at H = 0 is about 25 K, while T_{min} at H = 0.5 T is near 29 K. It should also be noted that the curvature of the R(T) dependence for the alloy films with and without external magnetic field are nearly the same. Recently, Lamba et al. [10] applied the theory of Anderson localization to the cluster compound and successfully explained the localization of the states near the Fermi level and the occurrence of ferromagnetism due to the localization. Indeed the preliminary band structure calculations using tight-binding linearized-muffin-tin-orbital method revealed the fact that the band structure of the ordered equiatomic CoAl alloy
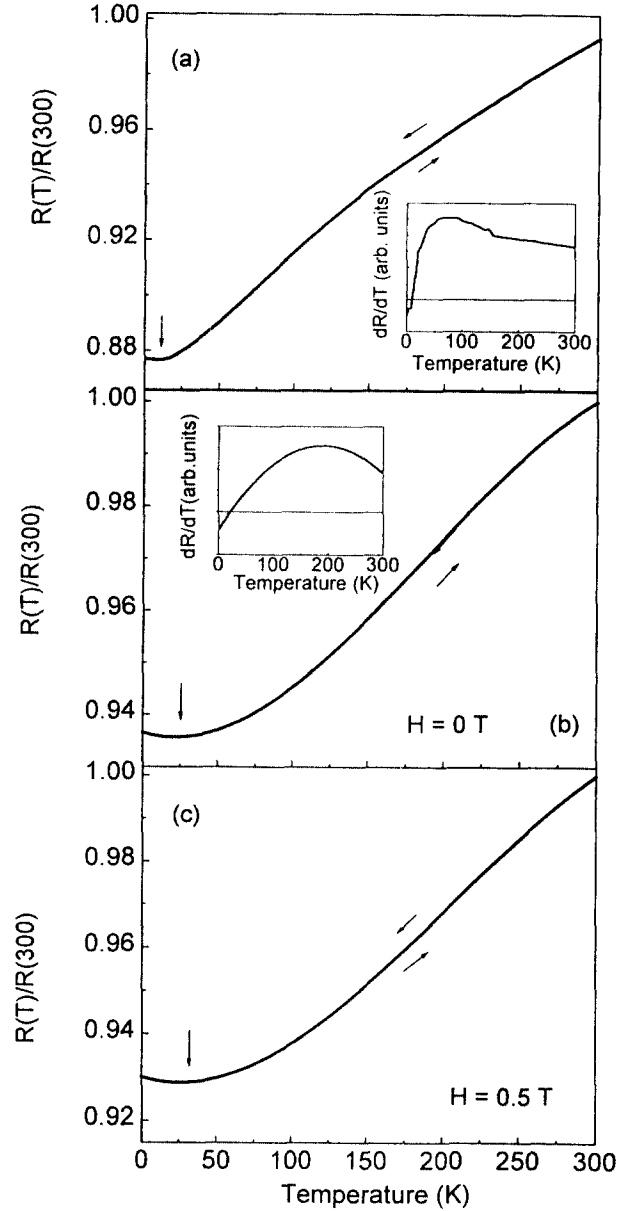

Fig. 4. Variation of the normalized resistance with temperature in zero [(a), (b)] and 0.5 T (c) external magnetic field for the ordered (a) and disordered [(b), (c)] $Co_{0.62}Al_{0.38}$ alloy films. Insets show the temperature derivatives of the resistance.

satisfies this. Therefore, we suggest that the upturn of the resistance at low temperature is caused by variable range hopping, in which the hopping mechanism dominates the charge transport.

4. CONCLUSIONS

The disordered state in the $Fe_{0.52}Al_{0.48}$ and $Co_{0.62}Al_{0.38}$ alloy films was obtained by means of vapor quenching deposition onto substrates cooled by liquid nitrogen. It was shown experimentally that the loss of the translational invariance in the disordered state leads to significant changes in its magnetic, MO and transport properties.

The observed changes in the MO properties caused by the order-disorder structural transition were discussed by using not only the EMA but the structural defect approach. The application of the computer simulation allowed to show that the MO properties of the Fe-ASA differ significantly from those of bulk Fe. The EKE spectrum of the disordered $Co_{0.62}Al_{0.38}$ alloy film shows the additional interband absorption whose shape in the spectrum is similar to that of the pure Co film. Therefore, we attribute this additional MO absorption and the EKE response of the disordered $Co_{0.62}Al_{0.38}$ alloy film to the bcc precipitates introduced into the matrix of CoAl alloy. The observed temperature and structural dependencies of T_{min} and the temperature dependence of the resistance at low temperature in the investigated $Co_{0.62}Al_{0.38}$ alloy films can be explained in terms of the partial localization of the electronic states and variable range hopping conductivity.

REFERENCES

1. B. I. Min, T. Oguchi, H. J. F. Jansen, and A. J. Freeman, J. Magn. Magn. Mater., **54-57**, 1091 (1986).
2. V. L. Moruzzi and P. M. Marcus, Phys. Rev. B, **47**, 7878 (1993).
3. R. B. Frankel, D. J. Sellmyer, and N. A. Blum, Phys. Lett., **33 A**, 13 (1970).
4. D. J. Sellmyer, G. R. Caskey, and J. J. Franz, J. Phys. Chem. Solids, **33**, 561 (1972).
5. E. Wachtel, V. Linse, and V. Gerold, J. Phys. Chem. Solids, **34**, 1461 (1973).
6. A. Amamou and F. Gautier, J. Phys. F : Metal Phys., **4**, 563 (1974).
7. F. A. Shavanov and I. V. Lezhnenko, Phys. Metal. Metallorg., **35**, 1119 (1973) and references therein.
8. Yu. V. Kudryavtsev, J. Dubowik, and F. Stobiecki, Thin Solid Films, 1995, **256**, 171 (1995).
9. D. Bagayoko, A. Ziegler, and J. Callaway, Phys. Rev. B, **27**, 7046 (1983).
10. S. Lamba, A. K. Rastogi, and D. Kumar, Phys. Rev. B, **56**, 3251 (1997).