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SOME RECENT ACHIEVMENTS IN AMORPHOUS MAGNETIC THIN FILMS[1]

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A brief survey of some recent achievments in the studies of magnetic properties of thin amorphous films or rare earth-transition metals (RE-TM) as well as of transition metal-metalloid (TM-M) alloys is presented.

О НЕКОТОРЫХ ПОСЛЕДНИХ ДОСТИЖЕНИЯХ В ОБЛАСТИ АМОРФНЫХ МАГНИТНЫХ ТОНКИХ ПЛЕНОК

В статье приводится краткий обзор результатов, полученных при изучении магнитных свойств аморфных тонких пленок сплавов типа редкоземельный металл – металл переходной группы и металл переходной группы – металлоид.

I. INTRODUCTION

The studies of magnetic thin films have a long tradition; they developed rapidly when in the sixties the permalloy films were expected to have a wide range of application in modern electronics. After a time of declining interest in thin magnetic films a new interest was revived when in the early seventies the amorphous films or the GdCo alloy with cylindrical domains were prepared. The interest was brought about by the possibility to apply such films in the bubble memory devices and for the socalled thermomagnetic writing. In the case new phenomena, which inspired the development of more fundamental studies, were observed (e. g. [1, 2]). At present the following questions are discussed: a. Stripe and bubble domains in amorphous Re—TM films b. Magnetization, anisotropy and other magnetic properties and their temperature dependences. c. Galvanomagnetic effects and electrical resistivity. d. The influence of annealing on magnetic properties of amorphous films. e, Structure of amorphous films, its thermal stability

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and phase transitions. f. The conditions of preparation of amorphous films and their influence on the structure and the magnetic properties.

Some of the above topics will be discussed in this survey.

II. STRUCTURE AND PHASE TRANSITION

The physical properties of thin film depend to a great extent on the arrangement of atoms in the material. That is the reason why the investigation of crystallographic structure of thin films are as old as the film studies in general. The construction of a theoretical model of amorphous solids with magnetic order requires a detailed knowledge of the atom distribution, on the distance between them, etc. Information on the atomic arrangement in amorphous solids is obtained from X-ray, electron and neutron scattering experiments and from density measurements. However, the latter are very difficult as regards thin films.

Amorphous solids are characterized by diffuse diffraction patterns with broad overlapping peaks. Scattering measurements can be used to obtain radial distribution functions (RDF's), which describe correlations among atomic positions. The RDF is not enough to give the coordinates of atoms, it rather gives an average information on correlations between atomic positions, e. g., the number of atoms of the first and the second neighbouring shell and the average distance of the first and the second nearest neighbours. RDF's exhibit several differences between the atomic arrangements in amorphous and crystalline alloys [3]:

a. The long range structural periodicity is absent in amorphous alloys; there are only a weak correlation between atomic position separated by more than four atomic diameters.

b. There is no unique nearest neighbours distance in the amorphous alloys. Widths of maxima in the RDF's range are between 0.4 and 0.5 Å, while for crystalline Fe, Co and Ni it is about 0.2 Å.

Density measurements indicate that atoms in amorphous TM-M alloys are quite densely packed together and crystallization increases their densities by only 0.5—1.0 %.

Most amorphous alloys are metastable at room temperature and recover their more stable crystalline state only when heated. Apart from the scattering methods, electrical resistivity measurements are very helpful in determining the amorphous-crystalline transition, because of the sudden decrease of the resistance at the crystallization of the alloy (Fig. 1).

Nanda and Grundy [10] used the electron diffraction technique to investigate the structure of thin, vapour quenched Gd—Co and Ho—Co films. The films became amorphous and metastable at room temperature. Investigations of the amorphous-crystalline transition in the series of vapour deposited thin films of RE-Fe and TM-B alloys have been reported by Dirks and Gijsbers [7]. Annealing and investigations were performed in the transmission electron microscope. All films possess a columnar microstructure in which the columns are surrounded by a network of alloy with a lower density. Heating of the RE-Fe films results in the formation of RE-oxides preferentially within the network. At the same time Fe-rich clusters are formed by a nucleation and growth mechanism. The crystallization ends at 970 K, when the columnar structure disappears. The TM-B films are more stable against oxidation and show a quite different crystallization behaviour. In the early stage of the amorphous-crystalline transition, precipitates are formed consisting of TM elements and TM borides. This nucleation and growth process is followed by a rapid transition of the remaining amorphous matrix to the crystalline state.

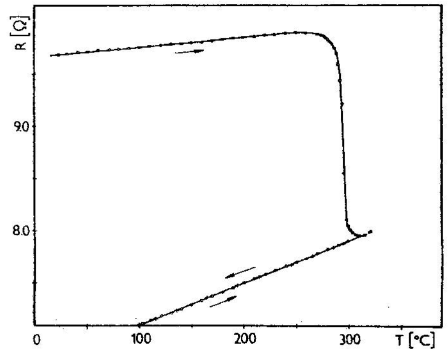

Fig. 1. Temperature dependence of the electrical resistivity of an amorphous $Co_{76}P_{24}$ thin film ([49]).

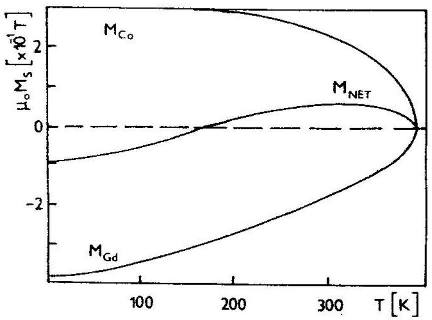

Fig. 2. The subnetwork and net magnetization for a Gd-Co thin film [28]).

The interpretation of the magnetic properties and the magnetic structure of amorphous alloys is complicated because there is not one single amorphous state, but rather a range of structures all of which are non-crystalline. This problem is considered in [5—9] and [11—15].

III. MAGNETIC PROPERTIES

Investigations of the magnetic properties of thin films are mostly related to their applications. In 1967 Bobeck [16] considered the possibility to create a bubble domain in the desired place of the sample and to move it in the sample plane [17]. This can be utilized in the construction of digital devices and magnetic storages for computers. Problems of application connected with the utilization of amorphous films as buble materials stimulated the development of futher studies of the magnetic properties of amorphous RE-TM thin films [18].

a. Magnetization

The considered amorphous RE-TM films are usually ferrimagnetics. It means that the net magnetization, M_s, of the alloy is a sum of the magnetization of the magnetic subblattices, which are antiferromagnetically coupled (Fig. 2). In consequence, the temperature dependence of M_s decreases to zero when the sublattice magnetization is equal to 0, i.e. $M_{RE} = M_{TM}$ (Fig. 3). This problem has hardly been examined in terms of the molecular field approximation (e. g. [18—21]. The change in magnetization is very strong near the compensation points. Even the perpendicular anisotropy, which is necessary for the occurrence of bubble domains, decreases drastically with increasing temperature (Fig. 4).

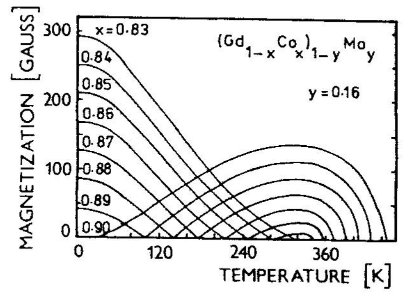

Fig. 3. Saturation magnetization as a function of temperature for different values of x ([20]).

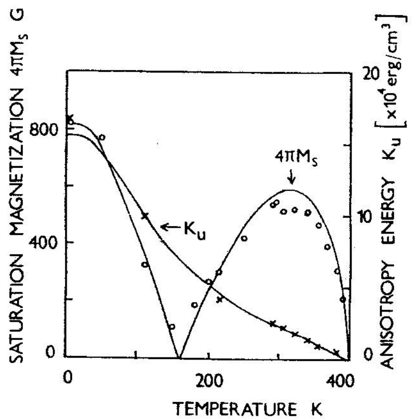

Fig. 4. Temperature dependence of saturation magnetization and anisotropy energy for a $Co_{62}Gd_9Mo_{14}Ar_{15}$ thin film ([50]).

b. The origin of the perpendicular magnetic anisotropy

Amorphous RE-TM films prepared by either evaporation or sputtering under certain condition exhibit an uniaxial magnetic anisotropy perpendicular to the plane of the film. If the anisotropy constant $K_u \ll 2\pi M_s^2$, the magnetization vector M_s lies in the film plane, because for this orientation the anisotropy energy becomes minimal (Fig. 5a). When $K_u > 2\pi M_s^2$, M_s is perpendicular to the film plane and stripe domains occur (Fig. 5b).

Originally one has expected no magnetic anisotropy in amorphous films since no preferred direction should exist in a truly amorphous solid. However, columnar structure has been observed in those films [7].

There have been a number of mechanisms proposed to explain the existence of perpendicular anisotropy in amorphous films, involving one or more of the following ideas: magnetocrystalline anisotropy, stress-induced anisotropy, shape anisotropy caused by some periodic fluctuation of composition, atomic short-range ordering.

In order to establish the most probable mechanism for creating perpendicular anisotropy, Hoffmann et al. [11] carried out the folowing studies:

Evaporated Gd—Co and Ho—Co films were prepared at 10^{-4} Pa on glass or NaCl substrate at room temperature. Sputtered Gd—Co films were also prepared by means of rf-bias sputtering with a basic voltage between 0 and − 130 V. Auger electron analysis of several films revealed that they contained some carbon and oxygen contaminations. The specimen surface showed qualitatively a depletion of

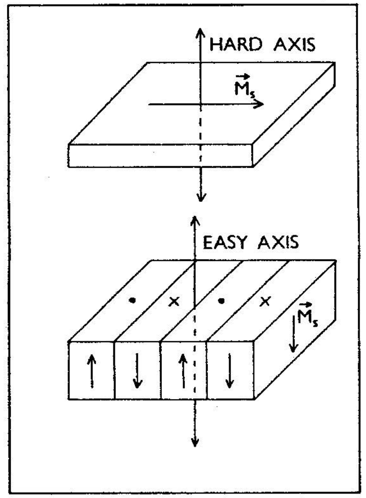

Fig. 5. The direction of M_s for different values of the anisotropy constant K_u

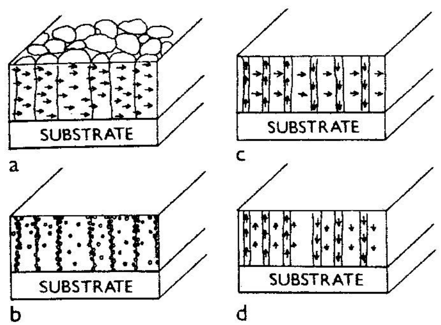

Fig. 6. The influence of the annealing on the domain structure of RE-TM thin film ([11]).

Co and an excess of Gd and 0. The samples were annealed at approximately 10^{-4} Pa for one hour in 40 or 50 K steps up to 1000 K. They were then examined by electron microscopy after each annealing stage. Both the evaporated and the sputtered samples were structuraly disordered when prepared. During annealing above 500 K, the diffraction rings became sharper and additional rings were observed. Full crystallization takes place between 790 and 870 K for the Gd—Co, and between 830 and 920 K for the Ho—Co films.

On the basis of Hoffmann's experiments the explanation of the anisotropy of evaporated as well as sputtered amorphous RE-TM films must be connected with the following factors: a. Anisotropic atomic short-range ordering. b. Influence of oxygen or other contaminations . c. Columnar structure of compositional inhomogeneities.

Due to the film growth a columnar structure of compositional inhomogeneities arises (Fig. 6a). The boundaries between the columns will favour oxygen diffusion from the surface towards the film interior. During annealing oxygen atoms will follow the very narrow path along the column boundaries and react with RE (Fig. 6b). Consequently the diffusion of oxygen is connected with the deactivation of the RE sublattice moment. This gives a number of non-compensated Co-pairs in the direction of the film normal (Fig. 6c). This is followed by the rotation of the magnetization of the rest of the film, giving rise to perpendicular anisotropy (Fig. 6d).

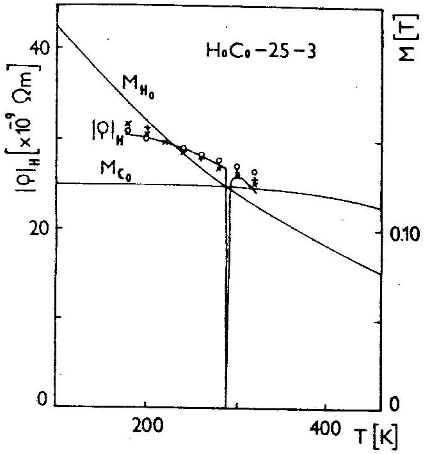

Fig. 7. Temperature dependence of the Hall resistivity of an amorphous Ho-Co thin film. ([34]).

c. Hall effect and magnetization reversal

Amorphous Gd-Co sputtered films with uniaxial magnetic anisotropy exhibit a very large anomalous Hall effect [22]. It was also found that hysteresis loops of the Hall voltage correspond to the *M-H* loops observed by the magneto-optical Kerr effect. That is why the Hall effect in amorphous RE-TM films is still being intensively studied [23—28].

The anomalous Hall effect is due to the magnetic ordering of spins in a ferromagnet. The effect is by about 2 or 3 orders of magnitude greater than the normal Hall effect. For TM the anomalous Hall effect is described in terms of the itinerant electron model taking into account a spin-orbit interaction responsible for the asymmetric scattering of the conduction electrons [29, 30]. On the basis of this model the extraordinary Hall coefficient $R_1 \sim \varrho^2$. It is supposed that R_1 is for TM

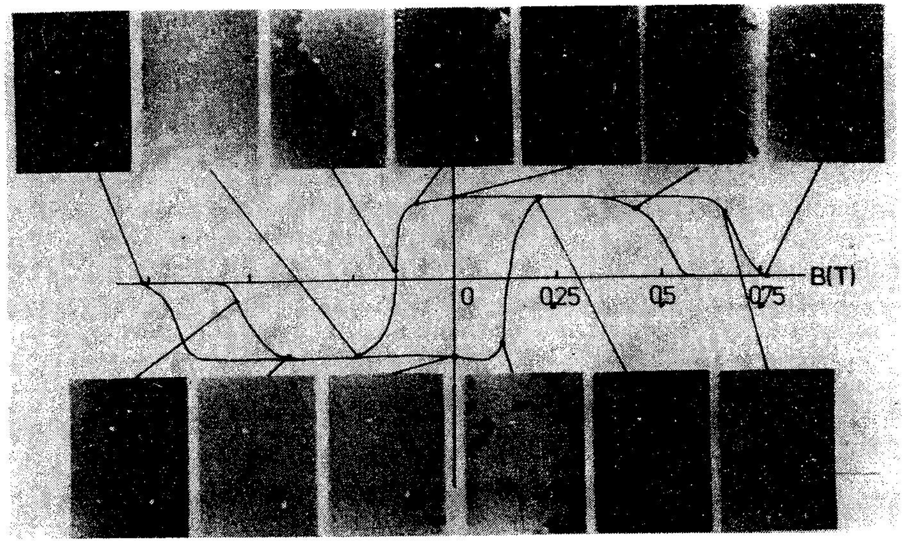

Fig. 8. Domain structure of a Ho-Co thin film at certain points of the hysteresis loop ([36]).

amorphous films almost temperature independent, similarly as the electrical resistivity ϱ. On the other hand, according to the localized electron model, R_1 would decrease with decreasing temperature [31—33].

It is generally assumed that the resultant Hall effect in RE-TM films should be related to every individual constituent separately. This supposition results from the change of the Hall voltage polarity at the compensation point T_{comp}. However, the results obtained by different authors exhibit considerable discrepancies.

On the basis of their study Ogawa et al. [23] conclude that in RE-TM film the dominant contribution to the Hall effect arises from the RE sublattice. Shirakawa et al. [25] showed on the contrary that the temperature dependence of the Hall voltage $|V_H(T)|$ and the TM sublattice moment $M_{TM}(T)$ are mutually proportional. This fact indicates that the TM sublattice plays a dominant role. Kobliska and Gangulee [28] found for Gd-Co films a satisfactory fitting of the expression

$$\varrho_H = n_0 \Sigma \langle R_{1i} \bar{M}_i \rangle \qquad (1)$$

for $R_{1Gd}/R_{1Co} = 1.25$. ϱ_H in equation (1) is the anomalous part of the Hall resistivity, $\langle\,\rangle$ denotes spatial averaging, $\bar{M}_i$ is the projection of M_i to the field direction for the i-th magnetic sublattice.

Using the same assumption as in [28], Ratajczak et al. [34] examined amorphous HoCo films. The obtained results are very close to those reported by

Kobliska and Gangulee (Fig. 7). It means that both components of the alloy have equivalent contributions to the Hall effect.

The Hall effect is very helpful in the study of the magnetization reversal process in the amorphous RE-TM thin films [35—37]. Anomalous hysteresis loops have been observed [38]. It was investigated whether a gradient of composition exists across the film thickness [39, 40], or whether regions of a different composition are present in the film. The observations of domain structure in definite points of the hysteresis loop (Fig. 8) did not confirm either the Esho model of the compositional gradient or the model of different composition regions.

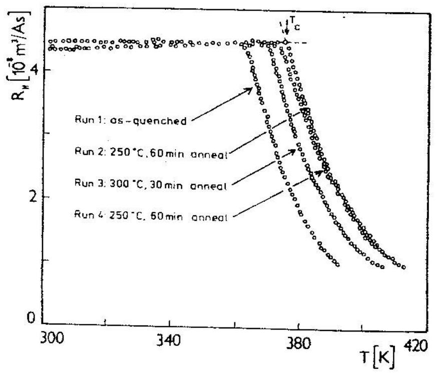

Fig. 9. The Hall voltage in an applied field of 0.022 T as a function of temperature for various annealing treatments of amorphous $Fe_{27}Ni_{53}P_{14}B_6$ ([13]).

d. Effect of annealing on the magnetic properties

As evident above, heating or annealing of amorphous films strongly affects their magnetic properties. Hence the problem of annealing effects is studied in many papers [6—11, 13—15, 41, 42].

The microscopic arrangements of atoms in amorphous solids are known to vary with the composition, the method of preparation and heat treatment. Malmhäll et al. [13] showed some consequences of the changes in compositional short-range order (CSRO) on the magnetic properties of the amorphous Fe—Ni—P—B alloy. Besides the structure sensitive parameters, such as coercive force and permeability, also the Curie temperature is influenced by annealing [43, 44]. Some Fe—Ni based amorphous alloys show a rather peculiar response to annealing, namely T_c after annealing first increase with increasing temperature and then is reduced. This behaviour was explained on the basis of the changes in CSRO [45]. The CSRO, principially of the nearest neighbours, can reach equilibrium in a much shorter time than the structural relaxations or crystallization. The measurements of the T_c variations were carried out by means of the Hall effect studies [13] (Fig. 9). The amorphous alloy obtained by rapid quenching retains the highly disordered CSRO

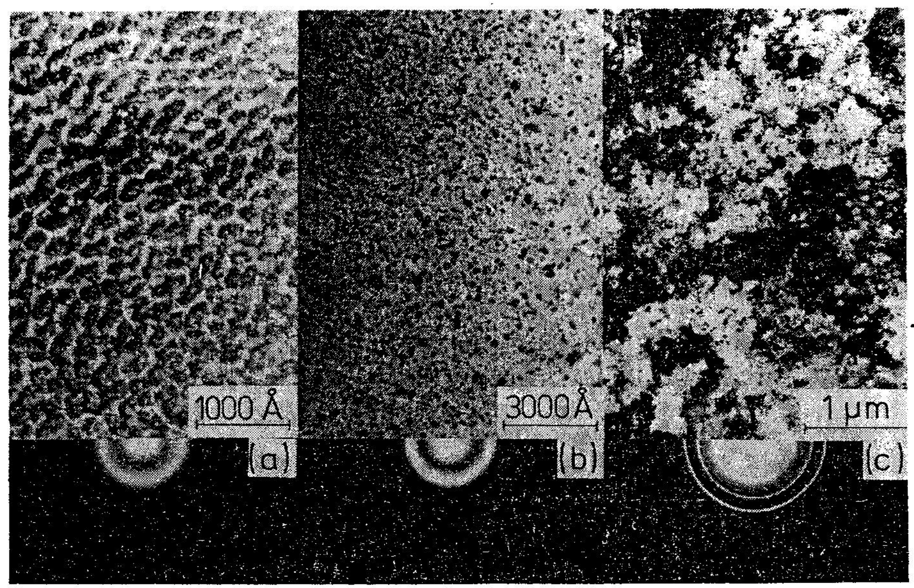

Fig. 10. Bright field micrographs and wide-angle diffraction patterns of a $Fe_{77}B_{23}$ sputter film, (a) as-deposited, (b) annealed at 730 K, (c) annealed at 770 K ([15]).

and shows a lower T_c. As the sample is annealed the short range diffusion begins to take place, The increase of T_c is therefore controlled by the kinetics of the diffusion.

The most frequently studied TM-M films are the Fe-B films, prepared by rf-sputtering [6, 7, 14, 15, 46—48]. The investigations of the structure and the magnetic properties of such films are reported in [14, 15]. The electron microscopy showed that as deposited films contain inhomogeneities with a period of about 200—400 Å, superposed by a faint structure (Fig. 10a). It may be due to compositional fluctuations and/or columnar structure with voids and pores, or to surface roughness. Annealing up to about 700 K does not cause any apparent changes in the film. The crystallization starts at about 700 K and crystallites with dimensions 100—200 Å are formed. (Fig. 10b). The complete crystallization takes place at about 770 K. Fig. 10c shows crystallites greater than 1000 Å in diameter and many sharp rings in the diffraction pattern. The crystalline film consists of a mixture of α-Fe and probably Fe_2B. The metastable phase Fe_3B could not be identified.

REFERENCES

[1] Chopra, K. L.: *Thin Films Phenomena*. McGraw-Hill Book Comp. New York, London 1969.
[2] Levy, R. A., Hasegawa, R. (Eds.): *Amorphous Magnetism II.*, Plenum Press, New York 1977.

[3] Cargill, G. S.: III. *Solid State Phys.* Academic Press, New York 1975.
[4] Luborsky, F. E.: J. Magn. and Magn. Mat. *7* (1978), 143.
[5] Kazama, N., Heiman, N.: J. Appl. Phys. *49* (1978), 1706.
[6] Shimada, Y., Kojima, H.: J. Appl. Phys. *50* (1979), 1541.
[7] Dirks, A. G., Gijsbers, J. R. M.: J. Phys. D: Appl. Phys. *12* (1979), 147.
[8] Hoffman, H., Winkler, R.: *Booklet of the Ninth Internat. Coll. Magn. Films and Surfaces.* Poznań 1979.
[9] Gościańska, I.: *Dissertation.* A. Miczkiewicz University, Poznań 1979.
[10] Nanda, S. S., Grundy, P. J.: J. Phys. F: Metal Phys. *7* (1977), 207.
[11] Hofmann, H., Owen, A. J., Schröpf, F.: Phys. Stat. Sol. (a) *52* (1979), 1.
[12] Müller, H. R.: Phys. Stat. Sol. (a) *49* (1978), K 63.
[13] Malmhäll, R., Bäckström, G., Rao, K. V., Egami, T.: J. Appl. Phys., *50* (1979), 7656.
[14] Schwarzl, S., Stobiecki, F., Hoffmann, H.: *Booklet of ICMFS-9*, Poznań 1979.
[15] Stobiecki, F., Schwarzl S., Stobiecki, T., Hoffmann, H.: 4^{th} *Int. Conf. on Liquid and Amorph. Metals,* Grenoble 1980, (to be published in J. Physique).
[16] Bobeck, H. A.: Bell Syst. Techn. J. *8* (1976), 1901.
[17] O'Dell, T. H.: *Magnetic Bubbles.* Macmillan, London 1974.
[18] Chandhari, R., Cuomo J. J., Gambino, R. J.: IBM J. Res. Develop. *17* (1973), 66.
[19] Hasegawa, R., Taylor, R. C.: J. Appl. Phys. *46* (1975), 3606.
[20] Hasegawa, R.: J. Appl. Phys. *46* (1975), 5263.
[21] Jouve, H., Rebouillat, J. R., Meyer, R.: AIP Nr. *29* (1975), 97.
[22] Okamoto, K., Shirakawa, T., Matsushita, S., Sakurai, Y.: IEEE Trans. Magn. *MAG-10* (1974), 799.
[23] Ogawa, A., Katayama–, T., Hirano, M., Tsushima, T.: AIP Conf. Proc. No *24* (1974), 575; Suppl. Japan J. Appl. Phys. *15* (1976), 87.
[24] McGuire, T. R., Taylor, R. C., Gambino, R. J.: AIP Conf. Proc. No *34* (1976), 346.
[25] Shirakawa, T., Nakajima, Y., Okamoto, K., Matsushita, S., Sakurai, Y.: AIP Conf. Proc. No *34* (1976), 349.
[26] Asomoza, R., Campbell, J. A., Jouve, H., Meyer, R.: J. Appl. Phys. *48* (1977), 3829.
[27] McGuire, T. R., Gambino, R. J., Taylor, R. C.: IEEE Trans. Magn. *MAG-13* (1977), 1598.
[28] Kobliska, R. J., Gangules, A.: *Amorphous Magnetism II,* Levy R. A., Hasegawa, R. Eds. Plenum Press, New York 1977.
[29] Karplus, R., Luttinger, J. M.: Phys. Rev. *95* ((1954), 1154.
[30] Luttinger, J. M.: Phys. Rev. *112* (1958), 739.
[31] Kondo, J.: Prog. Theor. Phys. *27* (1962), 772.
[32] Irkhin, Yu. P., Abelski, Sh.: Sov. Phys. Solid State *6* (1964), 1283.
[33] Maranzana, E. F.: Phys. Rev. *160* (1967), 421.
[34] Ratajczak, H., Gościańska, I., Szlaferek, A.: *Booklet of ICMFS-9* Poznań 1979.
[35] Lutes, O. S., Holmen, J. O., Kooyer, R. L., Aadband, O. S.: IEEE Trans. Magn., *Mag-13* (1977), 1615.
[36] Ratajczak, H., Gościańska, I.: Phys. Stat. Sol. (*in press*).
[37] Ratajczak, H., Labedzka, I.: Phys. Stat. Sol. *44* (1977), K 103.
[38] Ratajczak, H., Labedzka, I.: *Proc. of Conf. SMM-3,* Bratislava 1977.
[39] Esho, S.: Suppl. J. Appl. Phys. *15* (1976), 93
[40] Müller, H. R., Knappe, B., Kosicik, R., Roseman, P., Schmidt, D., Funke, A.: Phys. Stat. Sol. *36* (1976), 617.
[41] Cziraki, A., Fogarassy, B., Bakonyi, I., Tompa, K., Bagi, T., Hegedüs, Z.: 4^{th} *Int. Conf. Liquid and Amorphous Metals,* Grenoble 1980 (to be published in J. Physique).
[42] Graczyk, J. F.: IEEE Trans. Magn. *MAG-16* (1980), 35.

[43] Liebermann, H. H., Graham, C. D., Flanders, P. J.: IEEE Trans. Magn. *MAG-13* (1977), 1541.
[44] Chen, H. S., Sherwood, R. C., György, E. M.: IEEE Trans Magn. *MAG-13* (1977), 1538.
[45] Egami, T.: Mat. Res. Bull. *13* (1978), 557.
[46] Stobiecki, T., Hoffmann, H.: 4^{th} *Int. Conf. Liquid and Amorph. Metals,* Grenoble 1980 (to be publ. in J. Phys. C).
[47] Stobiecki, T., Stobiecki, F., Hoffmann, H: *Int. Conf. Metallic Glasses: Science and Technology,* Budapest 1980.
[48] Malozemoff, A. P., Fernangel, W., Brunsch, A.: J. Magnetism Mag. Mat. *12* (1979), 201.
[49] Konč, M., Szabó, J. D., Košturiak, A., Zagyi, B., Duša, O.: Acta Phys. Slov. *28* (1978), 57.
[50] Shirakawa, T., Okamoto, K., Onishi, K., Matsushita, S. Sakurai, Y: IEEE Trans. Magn. *MAG-10* (1974), 795.

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