OLVASÓTERMI PÉLDÁNY
TK 15J. 389

KFKI-1982-46

L. TAKÁCS
C. HARGITAI

HYPERFINE FIELDS AND LOCAL ENVIRONMENT IN IRON-BORON METALLIC GLASSES

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

2017

KFKI-1982-46

HYPERFINE FIELDS AND LOCAL ENVIRONMENT IN IRON-BORON METALLIC GLASSES

L. Takács and C. Hargitai

Central Research Institute for Physics
H-1525 Budapest 114, P.O.B.49, Hungary

Submitted to J.Phys.F: Metal Phys.

HU ISSN 0368 5330
ISBN 963 371 932 1

ABSTRACT

The concentration dependence of the average hyperfine field and the hyperfine field distribution in $Fe_{100-x}B_x$ metallic glasses ($0 \leq x \leq 25$) is explained in terms of a local environment model based on "dense random packing of hard spheres" model structures. It is assumed that the hyperfine field at iron sites without boron neighbours is sensitive to local compression or dilation in analogy to crystalline close-packed iron. In this way even the strong decrease of the average hyperfine field at low boron content can be explained.

АННОТАЦИЯ

Объяснена концентрационная зависимость средней величины и распределения сверхтонкого поля в аморфных сплавах $Fe_{100-x}B_x$ ($0 \leq x \leq 25$) с помощью модели "локальное окружение". Необходимая структурная информация получена из модели со случайной плотнейшей упаковкой жестких шаров. Предполагалось, что в случае атомов железа, не имеющих по соседству бора, сверхтонкое поле зависит от локального стягивания и расширения, подобно случаю плотнейшей упаковки кристаллического железа. Таким образом можно было объяснить даже сильное снижение средней величины сверхтонкого поля в случае малых концентраций бора.

KIVONAT

Az átlagos hiperfinom tér és a hiperfinom tér eloszlás $Fe_{100-x}B_x$ ($0 \leq x \leq 25$) fémüvegeken mért koncentrációfüggését egy lokális környezet modell segitségével magyaráztuk. A szükséges szerkezeti információt egy "véletlen szoros illeszkedésü" merev gömbökből álló modell szerkezetből nyertük. Feltételeztük, hogy a bór szomszédokkal nem rendelkező vas helyeken a hiperfinom tér a helyi kitágulásra vagy összenyomódásra érzékeny, hasonlóan a szoros illeszkedésü kristályos vas viselkedéséhez. Ilymódon az átlagos hiperfinom tér kis bór tartalomnál fellépő erős csökkenése is magyarázható volt.

1. INTRODUCTION

Hyperfine field distribution measurements are often regarded as an excellent additional tool to get information on the structure of metallic glasses. The connection between structure and hyperfine field is, however, indirect and within reliable limits each structural model could be brought into correspondence with the experimental hyperfine field distributions of Fe-B metallic glasses. Gonser et al. (1978) and Wagner et al. (1980) used hyperfine field distribution to support the dense random packing model; Vincze et al. (1979) and Kemény et al. (1979) referred to a quasi-crystalline model based on a "locally distorted off-stoichiometric" intermetallic compound; Fujita et al. (1977) and Oshima et al. (1981) used a supersaturated solid solution as a reference system; Dubois and Le Caer (1981) proposed a model built of trigonal prismatic molecules formed by a metalloid and its metal neighbours.

In trying to get unambiguous information on atomic structure, an important fact is ordinarily overlooked. Each of the considerations mentioned above gives a monotonically increasing average hyperfine field with decreasing metalloid concentration. This is indeed the case at relatively high metalloid concentrations (above about 10 at.% B in the case of $Fe_{100-x}B_x$) but at low concentrations the average hyperfine field drops

abruptly to about 20 T (Bjarman et al. 1980) instead of saturating near to the value measured in crystalline bcc iron. None of the previous model calculations have been able to reproduce this characteristic behaviour.

Our aim is to develop a local environment model for the hyperfine field distribution of iron-boron metallic glasses which can be used from pure amorphous iron up to at least 25 at.% boron concentration. To this end, we divide the iron sites into two classes:

(i) The hyperfine field at iron sites having some boron nearest neighbours is determined by the boron coordination number of the site. Apart from some subtleties, all the earlier studies are based, at least partially, on this assumption.

(ii) Iron sites with only iron nearest neighbours should be handled separately in a different way. For these sites a nearly close-packed local order is assumed and the hyperfine field is scaled to local compression or dilation analogously to the behaviour of crystalline close-packed (fcc) iron, where the hyperfine field (and the magnetic moment) is a function of the lattice parameter. The possibility of such an analogy has already been mentioned by Gonser (1980) but without any model calculations.

Though any kind of structural models can be used to calculate the hyperfine field distribution, in this paper we shall apply two component "dense random packing of hard spheres" model structures. This class of models is the one most used to describe structural features of amorphous

alloys but its applicability in explaining the concentration dependence of the magnetization and the hyperfine field has been questioned (Vincze 1979).

2. ASSUMPTIONS OF THE MODEL CALCULATIONS

a) The model structures

Due to the uncertainties in the relationship between local order and hyperfine field, quite different structural models can provide equally acceptable results. In view of this, one of the most generally used concepts "dense random packing of hard spheres" was applied here. The atomic diameters chosen for iron and boron atoms were 2.5 Å and 1.9 Å, respectively. The structure of amorphous pure iron was represented by the central part of a "geometrically relaxed" hard-sphere model built by Fukunaga and Suzuki (1981). In their model, the relaxation starts from a model structure generated by Ichikawa's algorithm. The geometrical relaxation procedure then moves the atoms one by one towards the centre of mass of their nearest neighbours. In this way the rearrangement of the spheres is achived without assuming any arbitrary pair potential. The structures of binary alloys were represented by models built using a Monte Carlo algorithm (Takács 1978). A fixed number of balls with two different sizes were dumped into a rectangular box without regard for the occurring overlaps. After this the overlaps between pairs of balls were reduced repeatedly until a practically overlap-free state was reached. Meanwhile, the distance between the

smaller balls representing the metalloid atoms were increased to avoid metalloid-metalloid nearest neighbours.

b) Relation between local order and the hyperfine field

It is generally accepted that the hyperfine field at an iron nucleus in Fe-B metallic glasses primarily depends on the metalloid coordination number. Thus, the definition of coordination numbers is of basic importance. The average coordination number can be calculated relatively easily by counting the number of atoms within a given distance from the central atom. However, this kind of definition of coordination number has disadvantages when looking at individual sites or coordination number distributions. The distance of neighbours from a given atom often increases so gradually that a natural cut-off distance for counting nearest neighbours cannot be defined and relatively minor distortions of the structure can cause abrupt changes of the coordination numbers. Moreover, the cut-off distance is somewhat arbitrary so that it is a hidden adjustable parameter.

A rather attractive way to define coordination number in materials with low symmetry has been adopted here (Carter 1976). First the Voronoi polyhedron of each larger ball was determined. (Instead of bisector planes, the planes between balls with different sizes were drawn at distances proportional to the diameters.) Then the quantity

$$Z = \left[\sum_i \left(\frac{V_i}{V} \right)^2 \right]^{-1} \qquad (1)$$

was used as the total coordination number. (V is the volume of the Voronoi polyhedron, V_i is the pyramidal volume contribution of the i-th neighbour, the sum stands for all the

neighbours defining the faces of the polyhedron.) If all the volume contributions are equal, Z is identical to the usual coordination number. Otherwise the contribution of the neighbours is weighted by the pyramidal volumes V_i. This coordination number changes continuously with any changes in the local geometry. The boron coordination number is defined as

$$Z_B = Z \frac{\sum_B V_i}{V} , \qquad (2)$$

where in the numerator the summation goes over the boron neighbours.

Now, it is assumed that at iron sites having boron neighbours the hyperfine field depends linearly on the number of boron neighbours

$$H = H_o - \alpha Z_B . \qquad (3)$$

The parameters H_o and α are to be determined in the following section. A closely related way to apply a continuous coordination number to establish a relation between local order and hyperfine field was proposed by Lines (1980).

The iron sites without boron neighbours, on the other hand, are treated in a completely different way. The reason for this is that at very low metalloid concentrations, i.e. at very small metalloid average coordination numbers, both the average magnetization and the hyperfine field at iron sites in amorphous iron-based alloys decrease and extrapolate to slightly above half the values measured in α-Fe. The exact values are rather uncertain because they are very sensitive to impurities and uncontrolled impurities are always present, even in nominally pure vacuum deposited or sputtered films.

However, this bahaviour is well established qualitatively (Wright 1976) and it can even be seen as a maximum of the average magnetization and hyperfine field at iron sites at about 10 at.% B in $Fe_{100-x}B_x$ alloys (Fukamichi et al. 1978, Dubois and Le Cear 1981).

Regarding the amorphous metals as "dense random packed" structures, it is natural to look for analogies between the magnetic properties of the amorphous and the close-packed (fcc) crystalline phases. The magnetic state of fcc iron is very sensitive to the lattice parameter. At larger atomic distances the iron moments increase in the case of all known modifications and the magnetic moments are reduced by the decreasing atomic distance. Moreover, in the close packed modifications (fcc and hcp) they can even vanish (Andersen et al. 1977). In analogy with this, let us suppose that in the amorphous alloys the hyperfine field at iron sites without boron neighbours is scaled to $\frac{V}{Z}$, the average Voronoi volume belonging to one neighbour. This is, perhaps, the least artifical analogue of atomic distance in the crystalline metal so the hyperfine field at iron sites with $Z_B=0$ is assumed to be

$$H = H_1 + \beta\frac{V}{Z} \qquad (4)$$

H_1 and β are parameters to be determined. $\beta>0$ is expected in accord with the lattice parameter dependence in fcc iron.

It is important to emphasize that a crucial assumption was made when the distance sensitivity of the magnetic moment in fcc iron - a very collective phenomenon - was used as an analogy for the establishment of a local environment model.

Nevertheless, it is hoped that this principle is basically correct even if the details are dubious. This problem is always present in local environment models - perhaps generally in less sensitive forms.

3. CALCULATION OF THE HYPERFINE FIELD DISTRIBUTION

In order to determine the hyperfine field distribution the following calculations should be executed:

(i) The distribution of Z_B and - for sites with $Z_B=0$ - that of $\frac{V}{Z}$ should be determined.

(ii) These distributions should be converted into hyperfine field distribution by using relations (3) and (4).

The first task can be performed in a straightforward manner using the atomic coordinates of the model structures. To cope with the second, however, our four parameters H_o, α, H_1 and β should be fitted.

H_1 and β describe the hyperfine field at the iron atoms surrounded exclusively by iron neighbours. The number of such sites is relatively low - less than 25% even at 12 at.% boron content - so H_1 and β are adjusted only to the hyperfine field distribution of nominally pure amorphous iron. As both the hyperfine field distribution and the distribution of $\frac{V}{Z}$ for the single component model structure is more or less symmetrical and a linear relation was assumed, it is enough to compare the average and the width of the distributions. From the model structure $\langle\frac{V}{Z}\rangle = 1.058$ Å^3 and $\sigma = 0.080$ Å^3 have been deduced for the average and the mean square deviation of $\frac{V}{Z}$. Comparing these data with $\bar{H} = 20$ T and $\sigma_H = 4$ T

(Bjarman et al. 1980) one can get H_1 = -32.9 T and σ=50 T/A^3. (As mentioned earlier, the values for $\bar{H}$ and σ_H are seriously influenced by impurities but as the weight of sites without boron neighbours is low, this uncertainty cannot substantially affect the resulsts for $x_B \geq 12$ at.%.)

The way to obtain H_o and α can be traced in Table I. First, the average $\frac{V}{Z}$ and the average hyperfine field h for the sites with $Z_B = 0$ are determined by using the parameters determined above. After this, the average hyperfine field H for the sites also having boron neighbours can be deduced by using the measured average hyperfine field $\bar{H}_m$, h and the number of atoms at the two types of sites. $\bar{Z}_B$ (the average boron coordination number of the sites with $Z_B > 0$) can also be onbtained from the model structures. The parameters H_o and α could be determined by fitting a straight line to the five (Z_B, H) points in Table I. In order to increase the number of points and to improve the consistency with the hyperfine fields measured in crystalline iron borides, five further points referring to the lattice sites occurring in Fe_3B, Fe_2B and FeB are added (Table II). To draw the Voronoi polyhedra the same diameter ratio has been assumed as used in the hard sphere models. In the case of Fe_3B the atomic coordinates of Ni_3P have been used assuming that the local order is not seriously different from that of Fe_3B. Since a linear relation has been assumed in eq. (3), H_o and α can be calculated by fitting a straight line to the average values in Table I and the local values in Table II simultaneously. In this way H_o = 35.4 T and α = 2.99 T have been obtained.

Now, using the parameters determined above, the average hyperfine field and the hyperfine field distribution can be calculated by using relations (3) and (4). The results are compared with the experimental data measured at 4 K by Dubois and Le Caer (1981) in Figs. 1 and 2.

4. DISCUSSION

The concentration dependence of the average hyperfine field (Fig. 1) shows that the main objective of the present considerations, i.e. the development of a local environment model which is able to reproduce the break-down of the average hyperfine field at low metalloid concentrations, could be achieved. Our starting point was the formulation of the analogy between pure amorphous iron and close-packed crystalline iron. The extreme distance sensitivity of the magnetic moment in the vicinity of the iron-iron nearest neighbour distance in the amorphous phase was assumed to be the most important common cause of the peculiar magnetic properties. However, any such kind of calculation is necessarily a rough simplification which can cover the main phenomena but not the exact details.

An important assumption to explain the observed decrease of the average hyperfine field at low metalloid concentrations was that the local order around iron atoms resembles a close-packed surrounding rather than a bcc one. This is in contrast with the model of Fujita et al. (1977) who assumes that the short-range order of amorphous alloys is very close to that of bcc alloys. If this were so the average

hyperfine field should increase to the value observed in α-Fe with decreasing boron concentration, but this is not the case.

By an appropriate choice of H/μ, the concentration dependence of the average magnetic moment μ could be fitted to the measured values but nothing new could be obtained compared with the tendencies of the average hyperfine field (Lines 1980).

Comparing the experimental and theoretical hyperfine field distributions (Fig. 2) two characteristics should be discussed:

(i) The global width of the distributions is similar. The agreement is especially convincing at the highest boron content. On decreasing the boron concentration a low field tail appears both on the experimental and theoretical curves. This peculiarity is more pronounced on the theoretical curves but taking into consideration the wide concentration range we are investigating, this deviation does not seem to be too considerable.

(ii) Contrary to integer coordination numbers, the use of the definitions given by relations (1) and (2) enables us to underline the importance of the fine structure in the calculated hyperfine field distribution. In principle, the coordination number and the hyperfine field could have a smooth, structureless distribution. The fact that this is not the case shows that the model structures are not completely random but different kinds of sites can be well separated. As the coordination numbers used here are calculated according to the different dimensions of the Voronoi polyhedra, they

are sensitive not only to chemical but also to topological short-range order. The hyperfine field distribution could be smoothed referring to those features of the atomic and magnetic structure which are not taken into consideration by Z_B or $\frac{V}{Z}$. Such features are the metal coordination number, the effect of farther neighbours and the magnetic moment of the neighbouring atoms. However, the calculated hyperfine field distributions shown in Fig. 2 are smoothed by an 0.8 T wide Gaussian curve simply to suppress statistical fluctuations but not to blot out the fine structure dictated by the distribution of the boron coordination number. Similar humps have also been found experimentally (Dubois and Le Caer 1981).

Finally, it should be emphasized once more that hyperfine field distribution should not be taken as a completely effective tool for distinguishing between the validity of different structural models. However, our calculation shows that dense random packing models - the most commonly used models to describe atomic structure and to explain physical properties - are at least not inconsistent with the global shape or the existence of a fine structure of the hyperfine field distributions.

The applicability of hyperfine field distribution for studying local order is greatly reduced by the fact that iron based metallic glasses are not strong ferromagnets (Takács 1979) so the local magnetic moment depends on the number of the 3d electrons as well as on the energy difference between the spin-up and spin-down states. If it is assumed that the boron coordination number determines the number of 3d electrons and the exchange interaction with the

magnetic neighnours determines the energy difference between the $3d\uparrow$ and the $3d\downarrow$ states, strong ferromagnets like cobalt based metallic glasses become more promising. In the latter cases the local magnetic moments and the dominant local contributions to the hyperfine field depend only on the occupation of the 3d states, thereby providing a more direct connection between hyperfine field and metalloid coordination number than for iron based metallic glasses.

REFERENCES

Anderson O.K., Madsen J., Poulsen U.K., Jepsen O. and Kollár J.:
1977 Physica 86-88B 249

Bjarman S., Kamal R. and Wäppling R. 1980 J.Magn.Magn.Mat. 15-18 1389

Carter F.L. 1976 J. Less-Common Met. 47 157

Dubois J.M. and Le Cear G. 1981 in: Proc.Int.Conf. on Amorphous Systems Investigated by Nuclear Methods /Balatonfüred, Hungary/ Vol.II, p.729 /to be published in Nucl.Instr.Methods/

Fujita F.E., Masumoto T., Kitaguchi M. and Ura M. 1977 Jap. J. Appl.Phys. 16 1731

Fukumichi K., Kikuchi M., Hiroyoshi H. and Masumoto T. 1978 in: Rapidly Quenched Metals III /The Metals Society, London/ Vol.2, p. 117

Fukunaga T. and Suzuki K. 1981 Sci.Rep. RITU A29 153

Gonser U., Ghafari M. and Wagner H-G. 1978 J.Magn.Magn.Mat. 8 175

Gonser U. 1980 J.Physique 41 C1-51

Kemény T., Vincze I., Fogarassy B. and Arajs S. 1979 Phys. Rev. B20 476

Lines M.E. 1980 Solid State Commun. 36 457

Oshima R. and Fujita F.E. 1981 Jap.J.Appl.Phys. 20 1

Takács L. 1978 in: Amorphous Metallic Materials /Proc.Conf. in Smolenice, Czechoslovakia/ ed. Duhaj P. and Mrafko P. /VEDA Publishing House of the Slovak Acad. Sci., Bratislava, 1980/ p. 323

Takács L. 1979 Phys.Stat.Sol. /a/ 56 371

Vincze I., Boudreaux D.S. and Tegze M. 1979 Phys.Rev. B19 4896

Wagner H-G., Ghafari M., Gonser U. and Naka M. 1980 J.Physique 41 C8-199

Wright J.G. 1976 IEEE Trans.Magn. 12 95

x	N	n	$\bar{H}_m$	$\frac{V}{Z}$	h	$\bar{Z}_B$	H	H_{cal}	$\bar{H}_{cal}$
12	662	141	30.0	1.157	25.0	1.29	31.4	31.5	30.1
16	648	80	29.7	1.143	24.3	1.62	30.5	30.5	29.8
18	556	54	29.4	1.096	21.9	1.81	30.2	30.0	29.2
20	632	41	28.9	1.120	23.1	1.96	29.3	29.5	29.1
24	617	18	27.5	1.125	23.4	2.41	27.6	28.2	28.1

Table I

Data used to determine the adjustable parameters in relations (3) and (4). x is the boron concentration in at.%, N the total number of metal atoms in the model clusters, n the number of iron atoms without boron neighbours. $\bar{H}_m$ the average hyperfine field in Teslas measured by Dubois and Le Cear (1981) at 4 K. $\frac{V}{Z}$ is the average of the specific volume of the Voronoi polyhedron in A^3 and h the average hyperfine field determined by relation (4) for the sites with $Z_B = 0$, H the expected average hyperfine field for these sites. H_{cal} is calculated by fitting relation (3). $\bar{H}_{cal}$ is the calculated total average hyperfine field.

Compound	Site	Z_B	H_m	H_{cal}
Fe_3B	(2)	2.01	30.0	29.4
	(3)	2.72	27.5	27.3
	(4)	3.84	23.0	23.9
Fe_2B		3.91	24.6	23.7
FeB		7.58	12.7	12.7

Table II

Boron coordination numbers Z_B and experimental (H_m) and calculated (H_{cal}) hyperfine fields for the lattice sites in crystalline iron borides (see e.g. Vincze et al. 1979)

FIGURE CAPTIONS

Fig. 1 Calculated average hyperfine field (x——) as compared with the values measured at 4 K by Dubois and Le Cear (1981) (o----) for Fe-B metallic glasses. The hyperfine field for pure amorphous iron is taken from Bjarman et al. (1980).

Fig. 2 Hyperfine field distributions calculated for 12, 18 and 24 at.% (full line) compared with distributions measured at 4 K at 12, 17.5 and 25 at.% boron concentrations by Dubois and Le Cear (1981) (dashed line), respectively.

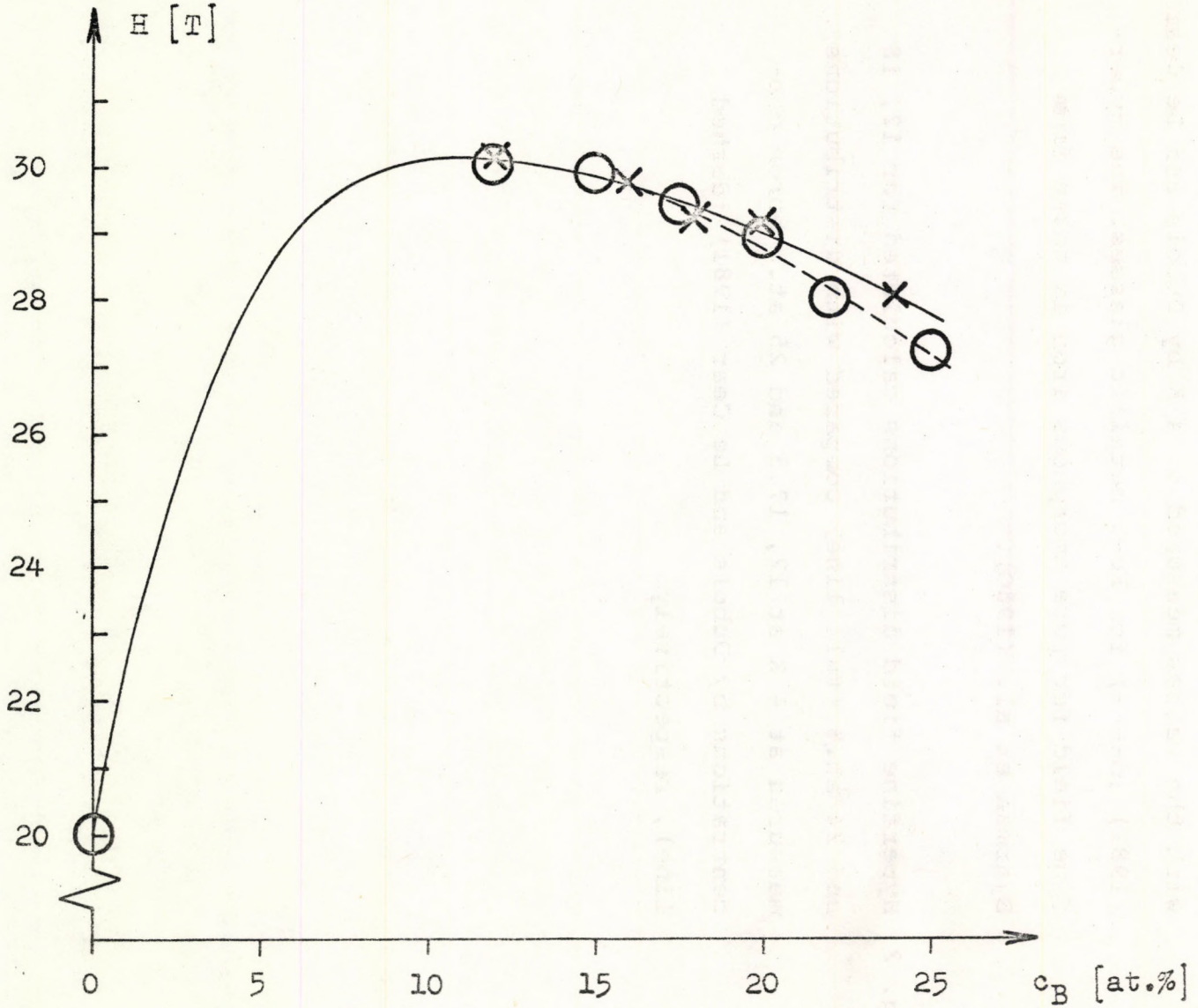


Fig. 1

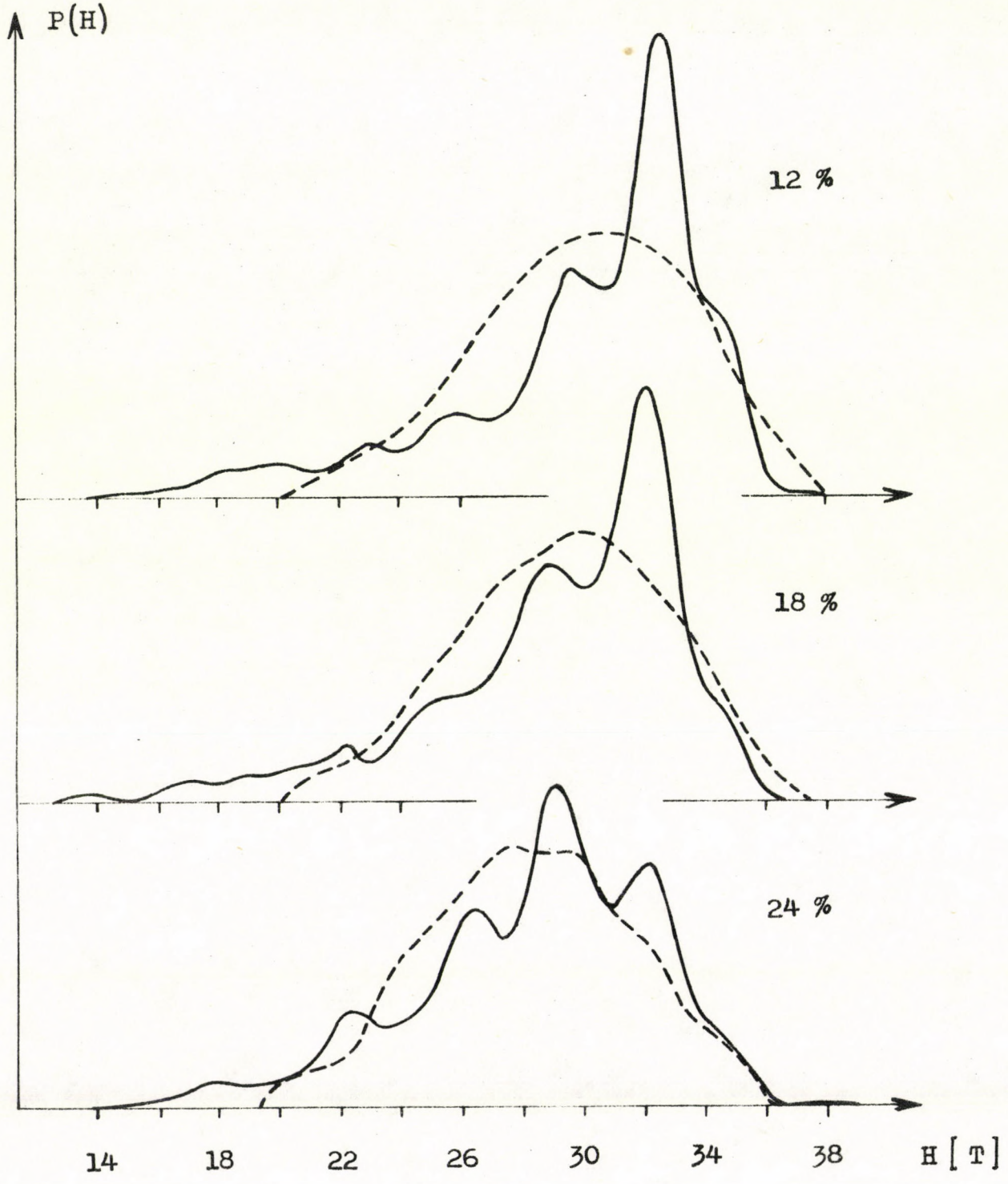
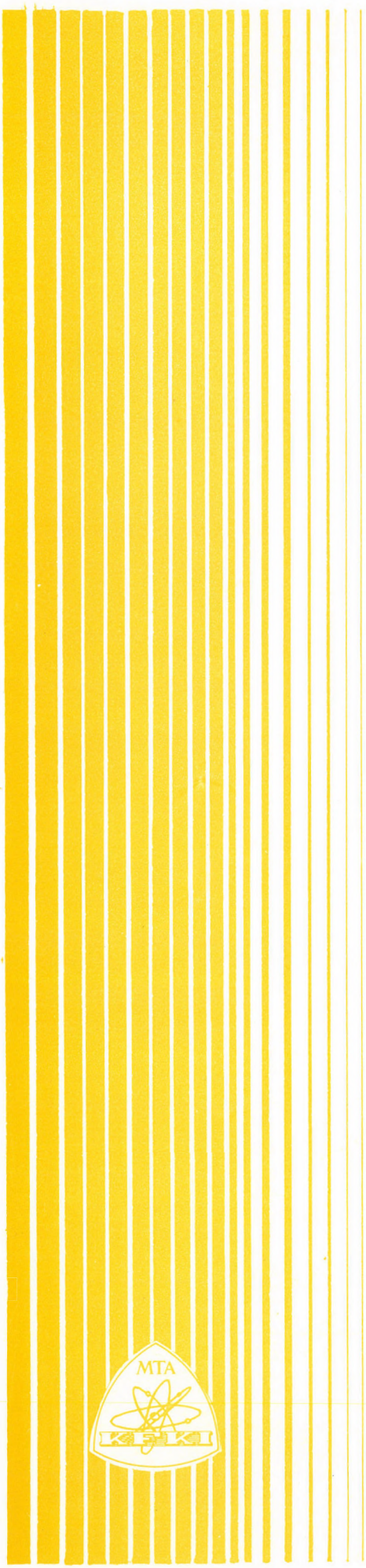


Fig. 2

63.260



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kroó Norbert
Szakmai lektor: Bakonyi Imre
Nyelvi lektor: Harvey Shenker
Gépelte: Beron Péterné
Példányszám: 325 Törzsszám: 82-376
Készült a KFKI sokszorositó üzemében
Felelős vezető: Nagy Károly
Budapest, 1982 junius hó