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ABSTRACT

Results of Mössbauer-measurements on the intermetallic compounds $(Fe_{1-x}Co_x)_2B$ $(0 \leq x < 1)$ and $(Fe_{1-x}Co_x)B$ $(0 \leq x \leq 0.5)$ are presented; the hyperfine field, isomer shift and quadrupole splitting being measured as a function of composition and temperature between 80°K and 1100°K. The data indicate that the electron states at iron sites are well-localized, and that iron keeps a nearly constant moment through the two ternary compound series. In $(Fe_{1-x}Co_x)_2B$ the nonlinearity of the magnetization versus concentration is attributed to an important change in the magnetic moments of cobalt atoms, moreover; the concentration and temperature dependence of the easy magnetization direction were also investigated.

РЕЗЮМЕ

Приводятся результаты измерений Мессбауэра, проведенных на интерметаллических сплавах $(Fe_{1-x}Co_x)_2B$ $(0 \leq x < 1)$ и $(Fe_{1-x}Co_x)B$; были измерены сверхтонкое поле, изомерный сдвиг, квадрупольное расщепление, в зависимости от состава и температуры в интервале температур между 80 и 1100°K. Данные показывают, что электронные состояния хорошо локализированы на местах железа, и что железо располагает близким к постоянному магнитным моментом в двух трехкомпонентных системах. В $(Fe_{1-x}Co_x)_2B$ нелинейность зависимости намагничиваемости от концентрации приписываем значительному изменению магнитного момента кобальта, кроме того исследовались зависимости направления легкого намагничивания от концентрации и от температуры.

KIVONAT

A $(Fe_{1-x}Co_x)_2B$ $(0 \leq x < 1)$ és $(Fe_{1-x}Co_x)B$ intermetallikus ötvözeteken végzett Mössbauer-mérések eredményeit közöljük; a hiperfinom teret, izomer shiftet és a kvadrupolus-felhasadást mértük az összetétel és a hőmérséklet függvényében 80 és 1100 °K között. Az adatok azt mutatják, hogy az elektronállapotok a vashelyeken jól-lokalizáltak, és hogy a vas közel állandó mágneses momentummal rendelkezik a két ternér rendszerben. $(Fe_{1-x}Co_x)_2B$-ban a mágnesezettség koncentrációfüggésének nonlinearitását a kobalt mágneses momentumok jelentős megváltozásának tulajdonitjuk, ezenkivül a könnyü mágnesezési irány koncentráció- és hőmérséklet-függését vizsgáltuk.

1. Introduction

The experimental data on interstitial compounds of transition metals with metalloids such as boron, carbon or nitrogen are often interpreted in terms of the so-called "donor model" in which the metalloid donates its valence electrons to the d-band of the metal (Lundquist, Myers and Westin 1962, Cadeville and Meyer 1962). The magnetic moment versus electron concentration curve of the isomorph series of T_2B and TB compounds with T=Cr, Mn, Fe, Co and Ni is very similar to the Slater-Pauling curve of the same transition alloys. The only difference is that the curve as a whole is shifted to the lower electron concentration by about 1.5 electrons for each boron atom. Similar results have been found by Kuentzler (1970) and Hanson, Mahning and Tóth (1971) from the low temperature specific heat measurements. However, as these types of measurement are sensitive to the bulk properties of the compounds, no detailed information on the mechanism of the electron transfer resulted. NMR and Mössbauer methods are suitable for investigating the details of the electron transfer since these give information about the charge and spin density distribution of theses systems.

The interaction between the transition metal 3d electrons and the metalloid s and p electrons may be studied in two different ways:

i. by substituting the metalloid with another metalloid with more or less electrons, or

ii. by leaving the metalloid unchanged and substituting the transition metal atom with another having a different overlap with the metalloid.

The Mössbauer-measurement on the $Fe_3(C_{1-x}B_x)$ cementite structure compounds carried out by Bernas, Campbell and Fruchart (1967) is the best example for the first type of experiment. One of their main experimental results was that the isomer shift was practically independent from of the average metalloid electron number.

The isomer shift reflects the change in the electron structure of iron atoms for it is proportional to the total s-electron density at the nucleus and thus depends on the total number of 4s and 3d electrons - indirectly through the screening of 3s electrons. It increases with the decrease in the number of 4s electrons or with the increase in the number of 3d electrons, however, the actual calibration has long been a bone of contention (see Fatseas (1973) and references given there).

The near constancy of the isomer shift in the $Fe_3(C_{1-x}B_x)$ system seemed to rule out the simple version of the donor model in which the iron gets some extra d-electrons at unchanged 4s configuration from the metalloid neighbours. As a matter of fact, the substitution of carbon by boron results in a decreased average sp electron number, i.e. the number of donated electrons to iron; and thus due to the reduced number of d-electrons, a decrease is expected in the isomer shift. On the other hand, the decrease in the average sp and d electron density giving a comparatively large positive contribution to the isomer shift compensating its above mentioned decrease (Fatseas 1973). In this case we wonder in which way this compensation takes place and whether it is characteristic only for this compound system with cementite structure. Unfortunately,

the number of such ternary series (with iron and two interstitial metalloids) is very limited and thus the above questions have not as yet been answered.

The second possibility is the investigation of ternary series in which the metalloid remains unchanged but the transition metal atom is substituted by another one. These systems are also important for the better understanding of the bonding and electron transfer to the metal atoms, expecially in view of the common band of the transition metal atoms. To our knowledge, apart from the very preliminary room temperature Mössbauer measurements of Cadeville et al. (1965) on a $(Fe_{0.6}Co_{0.4})_2B$ compound, no such type of investigation has been performed so far. We selected the $(Fe_{1-x}Co_x)_2B$ and $(Fe_{1-x}Co_x)B$ systems for our Mössbauer experiments since each system formed a solid solution across the whole concentration range. Moreover, the average magnetization of the $(Fe_{1-x}Co_x)B$ system decreases according to the simple dilution, whereas that for the $(Fe_{1-x}Co_x)_2B$ system shows a deviation upward from it. It is to be hoped that a much better understanding of the transition metal-metalloid interaction might be obtained by comparing the results of these two systems.

2. Experimental method and results

2.1 Apparatus

A conventional constant-acceleration Mössbauer spectrometer was used connected with a 1024 multichannel analyser and a 20 mCi ^{57}Co in chromium source. Within the measurements, the differential nonlinearity was found to be better than 0.1% and no measurable change of velocity or zero point could be observed

even during runs lasting several days. The spectra generally contained about $100\text{-}300\times10^3$ counts per channel collected during runs of 1-2 days. The measurements were carried out at temperatures from liquid nitrogen temperature to about 1100°K using a vacuum furnace above room temperature and a "cold finger" cryostat at low temperatures; the sample temperature was stabilized by temperature controller within ±1°C. Reproducibility was within the limits of experimental error.

2.2 Samples

The samples were prepared form 99.8% pure boron and 99.9% pure transition metals by induction melting under pure argon and homogenized by vacuum annealing. The homogeneity of the samples was checked by X-ray and all were found to be in a single phase. They all proved to be extremely hard but brittle so powders (grain size less than 50 m/u) were used for the Mössbauer measurements. The Mössbauer spectrum of the $(Fe_{0.5}Co_{0.5})B$ sample indicated the presence of a second phase (about 40% of the iron present), which was identified as $(Fe_{0.5}Co_{0.5})_2B$ on the basis of its Mössbauer parameters. The appearence of this phase was probably caused by the breaking operation. In the nomnally stoichiometric FeB sample a second six-line pattern (corresponding to 12% of the total iron content) was found which could be attributed to the presence of a samll boron excess originating from the sample preparation technique. During the preparation of pure FeB without traces of Fe_2B, namely, the respective proportions of Fe and B melted together were $Fe_{1-\varepsilon}B_{1+\varepsilon}$ with $\varepsilon\approx0.01$ to compensate the boron losses by evaporation or oxidation during the melting. The

concentrations of the samples were the following:

$(Fe_{1-x}Co_x)_2B$ with x=0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8;

$(Fe_{1-x}Co_x)B$ with x=0, 0.15, 0.35, 0.5 .

2.3 Evaluation of data and results

a. $(Fe_{1-x}Co_x)_2B$

Fe_2B and Co_2B have the same body-centred-tetragonal ($CuAl_2$-type) structure (Pearson 1967). In this structure the iron sites are crystallographically equivalent and in Fe_2B a typical iron atom has four symmetrically equivalent boron neighbours at a distance of 2.18 Å and 11 nearest iron neighbours as follows: the closest is at 2.40 Å, two atoms are at 2.45 Å, and there are two additional sets of four iron neighbours at distances of 2.69 and 2.72 Å. The magnetocrystalline anisotropy measurement of Iga et al. (1966) shows that at room temperature in Fe_2B the easy axis of magnetization lies in the plane perpendicular to the c-axis resulting in equal numbers of two non equivalent iron positions. Due to the anisotropic hyperfine interactions (magnetic and quadrupolar) the Mössbauer spectrum reflects the differences between these sites (Bernas and Campbell 1966, Weisman, Swartzendruber and Bennett 1969, Murphy and Hershkowitz 1973). The easy axis of magnetization was found by Iga et al. (1966) varying continuously between 518 and 524°K as a function of temperature, from its position in the c-plane into a position parallel to the c-axis. When the magnetization is along the c-axis all of the iron sites are magnetically equivalent as well and the Mössbauer spectrum really consists of a single six-line pattern: the room-temperature asymmetry disappears (Murphy

and Mershkowitz 1973). According to the Mössbauer measurements performed by these authors, the quadrupole splitting varies from $\Delta E=(+0.025\pm0.001)$ mm/sec to $\Delta E=(-0.037\pm0.003)$mm/sec in the temperature range 460 to 480°K but otherwise it is independent of the temperature. Evaluating ΔE, the electric field gradient tensor q was assumed to be axially symmetric, although this is not required by the crystal structure of Fe_2B, however, considering the analysis of the data this assumption does not appear to be very incorrect. In that case when magnetic hyperfine splitting is much larger than ΔE:

$$\Delta E = \frac{e^2qQ}{8}\left(3\cos^2\Theta - 1\right)$$

where the conventional notation is used. The observed change in the sign of ΔE was attributed to the change in the orientation of the easy axis of magnetization relative to the axis of the electric field gradient (the angle between them is Θ). Here a somewhat disturbing point remained, namely the transition proved to be more widespread and it occurred approximately 50°K lower than that obtained from the magnetocrystalline anisotropy measurement.

We reinvestigated the pure Fe_2B as a function of temperature and our results were generally in agreement with the previous investigations. The room temperature Mössbauer spectrum is shown in Fig 1. As a result of our better solution, the constraining assumptions on the equal isomer shifts, linewidths and intensities used earlier (Weisman, Swartzendruber and Bennett 1969) to fit the spectrum were obtained directly from the fitting of two independent six-line patterns. Here the equality of the two isomer shifts is of importance since the

crystallographical equivalence of the two types of iron sites is shown by it. The room temperature data are presented in Table I. The temperature dependence of the parameters was essentially the same as measured by Murphy and Hershkowitz (1973) with the exception that we found the change of the sign of the quadrupole splitting between 522 and 529°K in very good agreement with the magnetic measurements of Cadeville (1965) and Iga et al. (1966). Preliminary specific heat measurements suggest that the transition occurs at 527 ± 1 °K and its character is first order, the latent heat is 1.9 ± 0.3 cal/mole (T.Kemény, private communication). Thus the above mentioned 50°K discrepancy in the rotation temperature of the easy magnetization T_t is probably the consequence of the different sample preparation technique. The relative hyperfine field as a function of reduced temperature is shown in Fig 2. The resonant frequency of ^{11}B (Weisman, Swartzendruber and Bennett 1969) decreases a little faster than this curve, the deviation at room temperature is about 0.8%.

In Co_2B the behaviour of the easy axis of magnetization is just the opposite. At low temperatures it is along the c-axis and at about 70°K it rotates into the c-plane according to the magnetocrystalline anisotropy measurement of Iga (1966). The NMR investigation of Kasaya, Hihara and Koi (1973) shows an anisotropy splitting of the Co hyperfine field when the magnetization lies in the c-plane, one order of magnitude larger than in Fe_2B. This surprisingly large anisotropy of the Co atoms gives an extra interest to the study of $(Fe_{1-x}Co_x)_2B$ system.

Some typical room temperature Mössbauer spectra of

$(Fe_{1-x}Co_x)_2B$ are shown in Fig 1. The depth of the outer peaks on the figure generally reaches 60×10^3 counts per channel. The iron is not strongly affected by the Co substitution, only a line broadening about 20% was found. Due to this fact, the fit of a single six-line pattern to the spectra gave a reasonable good description, the reduced value of χ^2 $(= \chi^2/\langle\chi^2\rangle)$ was between 2.2 and 3.5 . The values of the room temperature Mössbauer parameters obtained from such a type of fit are listed in Table I. The main experimental results are the following:

i. the isomer shift is independent of the Co concentration (since the temperature dependence of the thermal shift is the same for each composition we can compare directly the room temperature values);

ii. the hyperfine field at iron atoms decreases very slowly for Co substitution, the total change of hyperfine field is $\frac{dH}{dc} = (-23.9 \pm 0.6)$ kOe;

iii. the quadrupole splitting is also independent of the Co neighbourhood (the apparent difference in the values is due to the fact that the easy magnetization axis is along the c-axis between x = 0.2 and 0.5, whereas it is again in the c-plane above x = 0.6);

iv. the temperature dependence of relative iron hyperfine field is the same as the function of reduced temperature independently of the Co concentration (Fig. 2);

v. the easy magnetization direction studied in the whole temperature range is along the c-axis for x = 0.2, 0.4 and 0.5 and in the c-plane for x = 0.7. For x = 0.6 above 570°K a rather smeared (attributed to the large Co con-

centration) transition from the parallel to the perpendicular (with the c-axis) state seems to start (the value of the quadrupole splitting decreases, e.g. $\Delta E=(0.009\pm0.006)$ mm/sec at $T = 670^{\circ}K$). Figure 3 shows the reorientation temperatures T_t and the Curie temperatures T_c measured by Cadeville (1965) and the present results as a function of concentration;

vi. the substitution of iron by cobalt affects the nearest three iron neighbours more strongly than the distant ones. The average decrease of iron hyperfine field due to a single Co atom is about -11.5 kOe. This conclusion is drawn from the analysis of the line shape in $(Fe_{0.6}Co_{0.4})_2B$ and $(Fe_{0.5}Co_{0.5})_2B$. In these compositions the easy magnetization direction is along the c-axis, each transition metal site is crystallographically and magnetically equivalent, thus the line broadening from the magnetic anisotropy is absent. The observed line broadening can be attributed to the random distribution of the Co atoms, and though the usual assumption of the additivity of hyperfine field changes and using the binomial distribution for the relative amplitude of a given configuration the change of the iron hyperfine field averaged over the different configurations due to the exchange of iron for cobalt can be determined. Here by assuming that only the three closest iron neighbours are affected by Co (i.e. the coordination number $z = 3$) a significantly better reduced chi-square value is given than by assuming that each of the 11 iron neighbours are perturbed by nearly the same extent ($\chi^2/\langle\chi^2\rangle = 1.2$ and 2.0, respectively).

The reliability of this fit is strengthened by the observation showing that for the two compositions the ΔH-s are the same within the experimental error (± 0.2 kOe). For z = 11 ΔH = -6 kOe was obtained . Furthermore, the increase in H_o (the hyperfine field of iron atoms without Co nearest neighbours) reflecting the effects of further Co neighbours is much smaller and more real when the assumption z = 3 is used $\left(\frac{dH}{dc}o = (+8 \pm 2)\text{kOe}\right)$, rather than z = 11 $\left(\frac{dH}{dc}o = (+40 \pm 2)\text{kOe}\right)$.

Obviously, this type of data evaluation cannot be used for x = 0.6, 0.7 and 0.8 since here an additional line broadening due to the magnetic anisotropy was observed;

vii. the quadrupole splitting in Fe_2B above the Curie temperature at 1083°K is $\Delta E = \frac{e^2qQ}{4} = (0.090 \pm 0.005)$ mm/sec; about half the value found by Murphy and Hershkowitz (1973). The reason for this discrepancy is unknown, but it is of importace considering the direction of q. Our value seems to be justified by the measurements performed on the mixed systems where similar quadrupole splitting values were found above the Curie temperatures. The value of $\Delta E = (-0.045 \pm 0.003)$ mm/sec above T_t in our experiment also differs from that of Murphy and Hershkowitz (1973).

Figure 4 shows the average magnetization for this series measured by Cadeville (1965), which does not follow the simple dilution.

b. $(Fe_{1-x}Co_x)B$

The FeB and CoB have the same orthorhombic B 27-type crystal structure (Pearson 1967) in which each transition metal atom is crystallographically equivalent, having six boron neighbours at 2.15 Å and ten iron or cobalt neighbours (six at 2.6-2.7 Å and four at about 2.9 Å). The transition metal atoms are magnetically equivalent since there is no sign of any magnetic anisotropy in the Mössbauer spectra, the data evaluation thus becomes simpler. The room temperature spectra are shown in Fig. 5. In the fitting of the spcetra we followed the same procedure as for $(Fe_{1-x}Co_x)_2B$):

i. the isomer shift is independent of the Co concentration;

ii. the iron hyperfine field decreases slowly at Co substitution: $\frac{dH}{dc} = (-8\pm5)$kOe at 80°K;

iii. the quadrupole splitting is independent of the Co neighbourhood and no sign of magnetic anisotropy was observed;

iv. the temperature dependence of the relative hyperfine field as a function of the reduced temperature is about the same as for $(Fe_{1-x}Co_x)_2B$ and is independent of the Co concentration (Fig. 2 shows the relative hyperfine field in FeB);

v. the quadrupole splitting above the Curie temperatures decreases with the increasing temperature of theses systems. We cannot differentiate between a temperature dependence proportional to T or T^2 because of the relatively small change in ΔE between T_c and 1000°K (about 0.03 $\frac{mm}{sec}$). A linear interpolation gives e.g.: $\frac{d\Delta E}{dT} = (-0.6\pm0.1)\times10^{-4}\ \frac{mm}{sec}\ {}^{o}K^{-1}$ and $(-0.7\pm0.1)\times10^{-4}\ \frac{mm}{sec}\ {}^{o}K^{-1}$; $\Delta E = \frac{e^2qQ}{4} = (0.244\pm0.009)\frac{mm}{sec}$ and $(0.286\pm0.004)\frac{mm}{sec}$ (extrapolated to 0°K) for x = 0 and 0.5, respectively.

The measured ΔE value in FeB just above the Curie temperature is in good agreement with that of Jeffries and Hershkowitz (1969);

vi. the line broadening caused by the Co substitution is much larger in this system than in $(Fe_{1-x}Co_x)_2B$ (e.g. the increase in the average linewidth is about 70% for 15 at% Co). The same decomposition technique used successfully to describe the increased linewidth in the $(Fe_{1-x}Co_x)_2B$ system was a failure in these compounds. Despite the relatively large decrease in the reduced χ^2 (about 1.7) the fit proved to be incosistent both for the z = 10 and 6 cases, as in contrast with the large increase in the hypefine field of the central line $\left(\frac{dH}{dc}\right)_0$ is about $+(50-70)$kOe) the decomposed linewidth remained unbroadened. Possibly these observations could be explained by a very angle-dependent hyperfine field perturbation with an average effect of nearly zero;

vii. the substitution of the iron neighbours by extra boron in FeB results in a large decrease of the iron hyperfine field, (-22.7 ± 0.5) kOe and a strong perturbation of the quadrupole splitting, while the isomer shift remains unchanged (Table II).

3. Discussion

Considering the idea of the common band of iron and cobalt in these compounds it is expected that each cobalt atom adds an extra electron to the common d-band, filling the spin up and spin down sub-bands. In this case the hyperfine field must be proportional to the total band magnetization actually

observed in the case of $Fe_3(C_{1-x}B_x)$ where obviously only a single band existed, or in the case of the $Y(Fe_{1-x}Co_x)_2$ Laves phase compounds which were much more similar to our case (Bernas, Campbell and Fruchart 1967, Guimaraes and Bunbury 1973). The proportionality constant was 130 and 155 kOeμ_B^{-1}, respectively.

The iron hyperfine field data presented in Table I and II clearly show that this requirement is not satisfied by our compounds. For example, in the $(Fe_{1-x}Co_x)_2B$ system the average magnetization predicts a total decrease of -150 kOe in the iron hyperfine field using the above mentioned values of the proportionality constant as opposed to the observed -25 kOe. Moreover, the concentration dependence of the average iron hyperfine field (which is linear) markedly differs from that of the average magnetization. The increase in the average magnetization of $(Fe_{1-x}Co_x)_2B$ above the simple dilution line could be explained as a first approximation, assuming a constant incerease in the iron moment or a constant decrease in the cobalt moment (or both) as a function of increasing cobalt concentration, i.e. $\mu_{Fe}(x)=\mu^{o}_{Fe} + x\Delta\mu_{Fe}$, $\mu_{Co}(x)=\mu^{o}_{Co} +(1-x)\Delta\mu_{Co}$. The fitted curve based on this model $\bar{\mu}_{calc}(x)=(1.907\pm0.001)-(0.68\pm0.02)x-(0.45\pm0.02)x^2$ is shown in Fig. 4 and is in a reasonably good agreement with the measured values. However, the observed change in the moments $\Delta\mu_{Fe} + \Delta\mu_{Co} = (0.45\pm0.02)\mu_B$ should be attributed to the decrease in the cobalt moment only $(i.e.\ \Delta\mu_{Fe} = 0)$ for the following reasons. In the $(Fe_{1-x}Co_x)B$ system the average magnetization decreases essentially according to the simple dilution. In agreement with this, the iron moment

remains unchanged and this fact is reflected in the nearly constant iron hyperfine field and the isomer shift. The isomer shift in the $(Fe_{1-x}Co_x)_2B$ system indicates that the iron is not perturbed by the Co substitution even in this case, whereas the small decrease in the hyperfine field can be attributed to the change in the transfer contribution of the nearest neighbours, since the conduction electron polarization contribution is supposed to have a small part in the hyperfine field of such systems (Bernas and Campbell 1967). The transfer contribution in the $(Fe_{1-x}Co_x)B$ system is probably much smaller due to the larger number of B neighbours which screen the iron more effectively, and to the larger distance of the transition metal neighbours. On the other hand, the large decrease in the iron hyperfine field in FeB due to the substitution of iron by extra boron is probably caused by the strong decrease in the magnetic moment of iron itsef (about $0.17\mu_B$) rather than by the change in the transfer hyperfine field contribution ($\frac{d\bar{\mu}}{dc} = -2.8\mu_B$/B atom is expected instead of $-1.1\mu_B$/B atom). Unfortunately, the average magnetization of the $Fe_{1-x}B_{1+x}$ system has not, to our knowledge, been investigated so far, although a similar strong decrease in the average magnetization has been observed, for example in the $FeBe_2$ system with extra Be($\frac{d\bar{\mu}}{dc} = -3.65\ \mu_B$/Be atom) by Herr, Kuentzler and Meyer (1969). The fact that despite the assumed considerable moment decrease the isomer shift of these iron atoms remains unchanged (whereas for Fe_2B the increase of the isomer shift is 0.12 mm/sec and the decrease of μ_{Fe} is $0.3\mu_B$) suggests that the mechanism of the moment decrease is not a simple donation of extra electrons into the iron 3d spin-down band, but a decrease in the magnetic

splitting of the 3d band due to the symmetry change. The increased asymmetry is reflected in the nearly doubled quadrupole splitting.

The similar temperature dependence of the hyperfine field (i.e. the magnetization) at iron in these systems, which is independent from the Co concentration indicates also a well-localized iron moment. The relative hyperfine field h_{Fe} decreases faster in $(Fe_{1-x}Co_x)_2B$ than in $(Fe_{1-x}Co_x)B$ as it is expected, if the Brillouin functions for spins 1 and 1/2 are compared - although the h_{Fe}-T/T_c curve is different from these functions.

A significant deviation from spherical symmetry in the charge distribution of iron atoms in Fe_2B was observed by Brown and Cox (1971) in their X-ray scattering measurement. This is reflected in the relatively large quadrupole splitting of the Mössbauer spectrum. Above T_c $q = 0.66 \times 10^{24}$ cm^{-3} is obtained for the electric field gradient, which is supposed to be axially symmetric and is comparable (about three times smaller) then the value of the more anisotropic Co_2B (Kasaya, Hihara and Koi 1973). The comparison of the quadrupole splitting data in the temperature range between T_t and T_c with that above T_c gives $\Theta = 90^\circ - 77^\circ$ for the angle between q and the c-axis the easy magnetization direction in this case. Below T_t the angle between the easy magnetization and q is $43^\circ \pm 2^\circ$ which together with the crystal symmetry seems to favour the easy axis of magnetization being parallel with the orthorhombic axis while the q is directed towards the closest iron neighbour in the c-plane. The about 10 kOe difference in the hyperfine field of iron atoms due to the anisotropy is by one

order of magnitude larger than the crystalline dipolar fields. Neutron scattering measurement (Brown and Cox 1971) indicates that the orbital magnetic moment is probably quenched due to the low symmetry of the crystal field at the iron sites. In this way, the anisotropy in the hyperfine field can be attributed to the dipolar field due to the spin moment of the 3d electrons inside the iron cell. Thus the electric field gradient and the dipolar field are expected to be proportional to each other (Perlow, Johnson and Marshall 1965) according to the relation:

$$H^d = \mu_B \, q(1-R)^{-1},$$

where μ_B is the Bohr magneton and R is the Sternheimer shielding factor. Using R = 0.3 as for Fe^{2+} ion (Ingalls 1964) H^d is 8.7 kOe in a strikingly good agreement with the measured value. This relation has also given a reasonable value of H^d in Co_2B (Kasaya, Hihara and Koi 1973).

The easy axis of magnetization at low temperatures lies in the c-plane in Fe_2B, whereas it is along the c-axis in Co_2B. Its direction is clearly connected with the anisotropic spin-density distribution of iron in Fe_2B found by neutron scattering (Brown and Cox 1971), which certainly differs from that of Co_2B. The very interesting concentration and temperature dependence of this direction in the $(Fe_{1-x}Co_x)_2B$ system is connected with the highly anisotropic interaction of iron and cobalt. In the absence of other data (lattice distortion, spin-density distribution) we cannot give a simple explanation for these experimental observations.

The observed temperature dependence of the quadrupole splitting in the paramagnetic state of $(Fe_{1-x}Co_x)B$ might

arise from the heat dilatation of the lattice and from the termal smearing of the Fermi level as suggested by Watson, Gossard and Yafet (1965). Each contribution results in a decrease of q; the first term is proportional to T, the second to T^2. On the basis of our experimental data we were not able to determine the exact function form of the temperature decrease of q. In the absence of any lattice dilatation measurement it is not possible to estimate the decrease arising from the lattice contribution of q. On the other hand, the conduction electron contribution due to q which is proportional to the density of electronic states at the Fermi energy seems to be small as the quadrupole splitting remains unchanged within the experimental error for 70% Co substitution in Fe_2B, whereas the electronic specific heat increases by 50 per cent (Kuentzler 1970).

4. Conclusions

The most important result of our measurements is that the rigid band model which has been widely used in order to explain the magnetic properties of such compounds is not appropriate for the $(Fe_{1-x}Co_x)_2B$ and $(Fe_{1-x}Co_x)B$ intermetallic systems. In both these systems the iron has proved to be well localized according to the hyperfine field, the isomer shift, and the quadrupole splitting data. On the other hand, comparing these results the nearly constant iron moment with the concentration dependence of the average magnetization in $(Fe_{1-x}Co_x)_2B$ suggest that the magnetic moment of cobalt increases with decreasing cobalt content. Preliminary NMR investigatigation on ^{59}Co confirms this assumption. A possible

origin for this increase in the cobalt moment could be the change in the hybridization of the cobalt 3d and boron sp electrons with the Co concentration. In this case it is necessary to take both of the d and s-bands into consideration for the theoretical description of these intermetallic systems which differs from the case of the corresponding transition metal alloys where a tight-binding single band model was sufficient (Hasegawa and Kanamori 1972).

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Table I.

Room temperature Mössbauer parameters in the $(Fe_{1-x}Co_x)_2B$. $\bar{H}$ is the average iron hyperfine field, ΔE is the quadrupole splitting, i is the isomer shift relative to pure iron. (I and II represent the two iron sites due to the magnetic anisotropy in Fe_2B ; the average values over these sites are also given). The measured Curie temperatures T_c and the average magnetization $\bar{\mu}$ values at 20°K (Cadeville 1965) are also given.

x		$\bar{H}$(kOe)	$\Delta E(\frac{mm}{sec})$	$i(\frac{mm}{sec})$	T_c(°K)	$\bar{\mu}(\mu_B)$
0	I.	242.0(2)	0.036(3)	0.119(3)	1015(5)	1.908
	II.	231.7(2)	0.021(3)	0.121(3)		
	av.	236.9(2)	0.028(3)	0.120(3)		
0.2		229.6(2)	-0.051(3)	0.123(3)	963(5)	1.72
0.4		226.8(2)	-0.059(3)	0.121(3)	914(5)	1.59
0.5		224.5(2)	-0.054(3)	0.121(3)	860(5)	1.46
0.6		223.1(2)	0.028(4)	0.119(4)	803(5)	1.34
0.7		217.9(2)	0.028(3)	0.118(4)	750(5)	1.22
0.8		208.3(3)	0.030(8)	0.108(9)	651(5)	1.08

Table II.

Mössbauer parameters in $(Fe_{1-x}Co_x)B$. The average iron hyperfine field $\bar{H}$ and quadrupole splitting ΔE at 80°K, and the isomer shift i (relative to iron) at room temperature are given.

(* represents the parameters of iron atoms with one boron neighbour at the iron sites). The measured Curie temperatures T_c and the average magnetization $\bar{\mu}$ values at 20°K (Cadeville 1965) are also given.

x	$\bar{H}$(kOe)	$\Delta E\left(\frac{mm}{sec}\right)$	$i\left(\frac{mm}{sec}\right)$	T_c (°K)	$\bar{\mu}(\mu_B)$
0	129.6(0.3)	0.061(2)	0.263(3)	593(5)	1.118
	* 106.9(0.7)	0.109(3)	0.263(5)		
0.15	129.3(0.6)	0.060(4)	0.259(4)	493(5)	0.95
0.35	124.9(0.7)	0.060(4)	0.275(9)	338(5)	0.73
0.5	99.0(0.7)	0.069(6)	0.258(4)	283(5)	0.55

Figure Captions

Fig. 1 Typical room temperature Mössbauer spectra in $(Fe_{1-x}Co_x)_2B$.

Fig. 2 The relative iron hyperfine field normalized to the values taken at liquid nitrogen temperature in $(Fe_{1-x}Co_x)_2B$ as a function of the reduced temperature. The similar curve in FeB is shown as well.

Fig. 3 Direction of easy magnetizetion axis in the $(Fe_{1-x}Co_x)_2B$: $\perp$ in the c-plane, $\parallel$ along the c-axis. The transition temperature between them is marked T_t. The figure includes the transition temperatures and Curie temperatures T_c measured by Cadeville (1965) and the T_t of Co_2B (Iga 1966).

Fig. 4 The average magnetization of $(Fe_{1-x}Co_x)_2B$ at 20°K (Cadeville 1965). The broken line corresponds to the simple dilution, the full line is a calculated one.

Fig. 5 Room temperature Mössbauer spectra in $(Fe_{1-x}Co_x)B$.

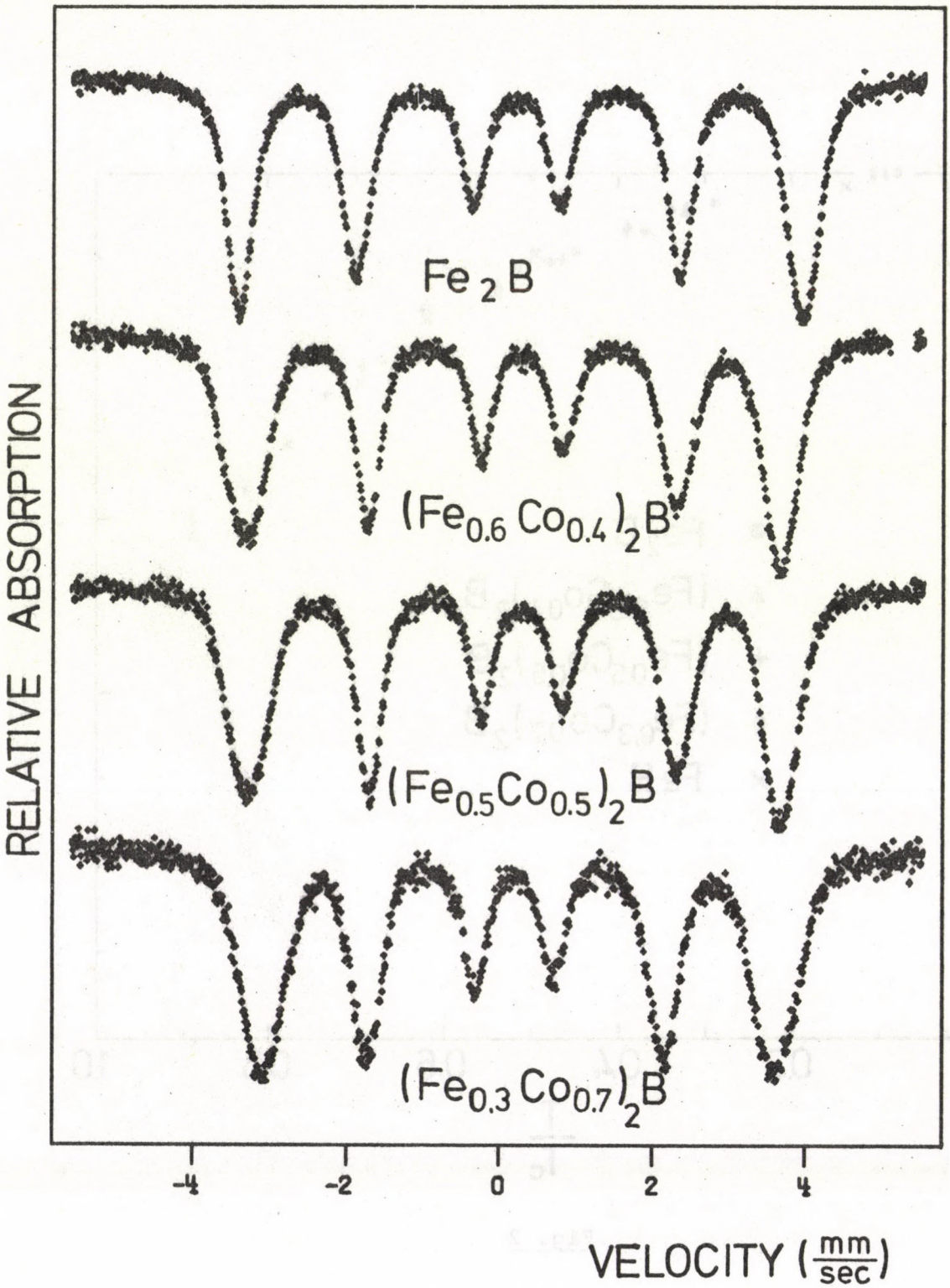

RELATIVE ABSORPTION
Fe2B
(Fe0.6 Co0.4)2B
(Fe0.5Co0.5)2B
(Fe0.3 Co0.7)2B
-4
-2
0
2
4
VELOCITY (mm/sec)

Fig. 1

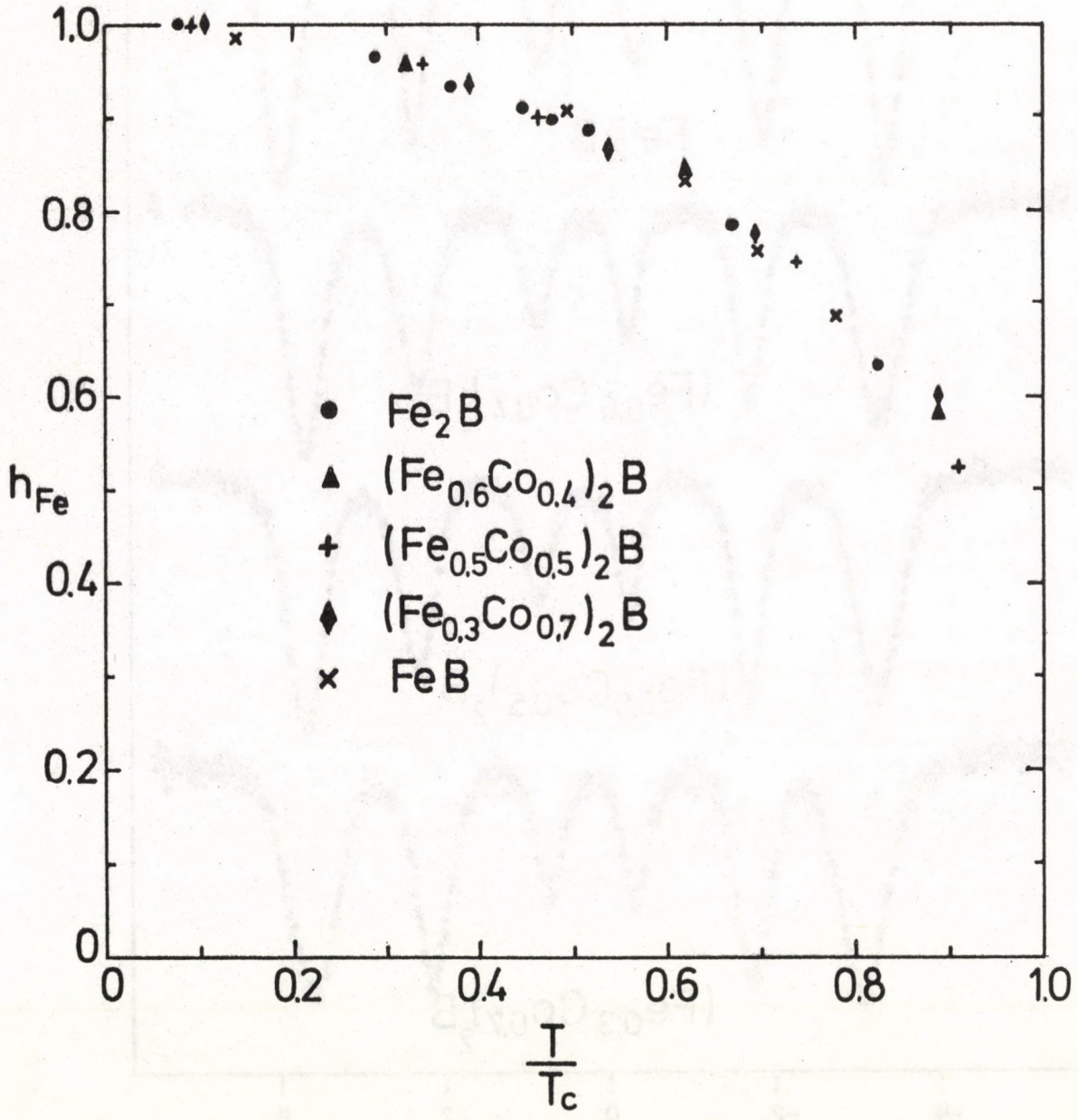

1.0
0.8
0.6
0.4
0.2
0
h_{Fe}
0
0.2
0.4
0.6
0.8
1.0
$\frac{T}{T_c}$
Fe_2B
$(Fe_{0.6}Co_{0.4})_2B$
$(Fe_{0.5}Co_{0.5})_2B$
$(Fe_{0.3}Co_{0.7})_2B$
FeB

Fig. 2

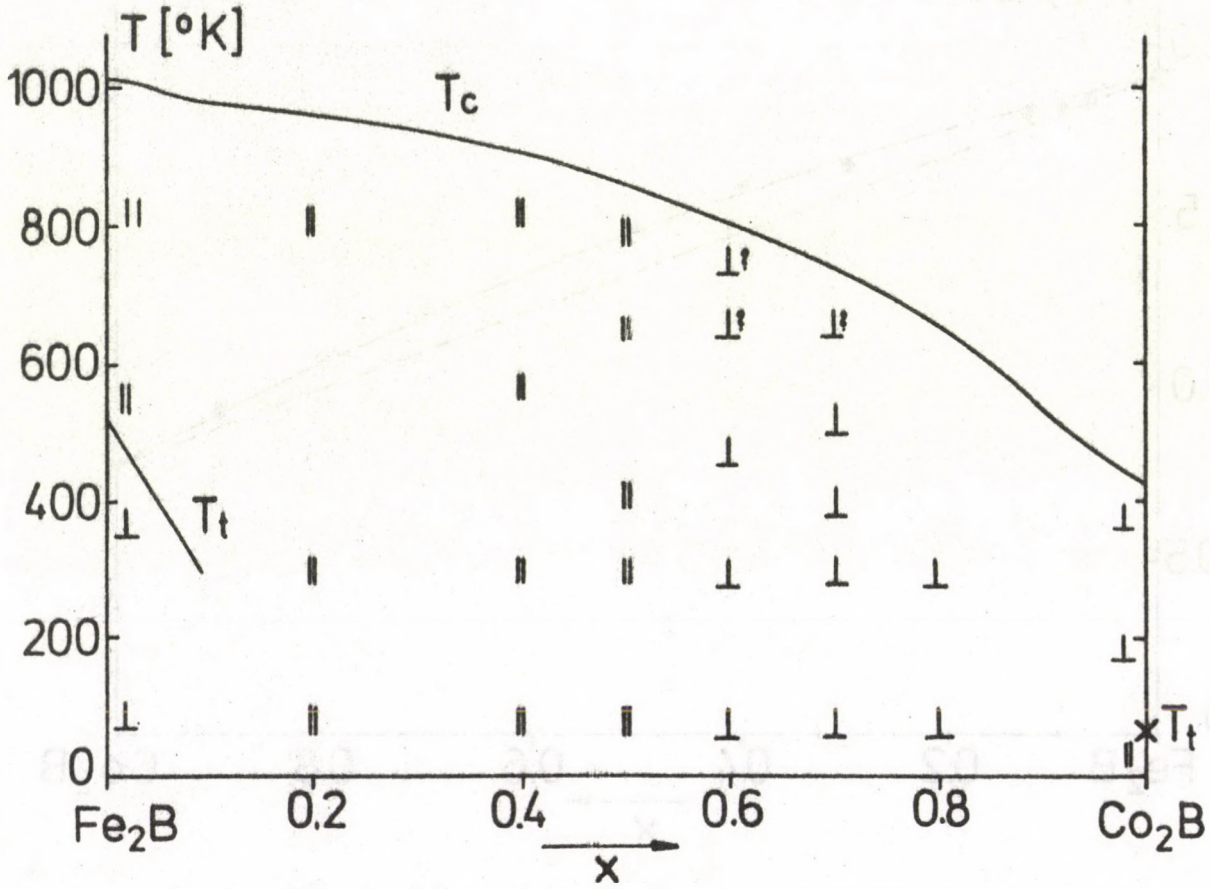


Fig. 3.

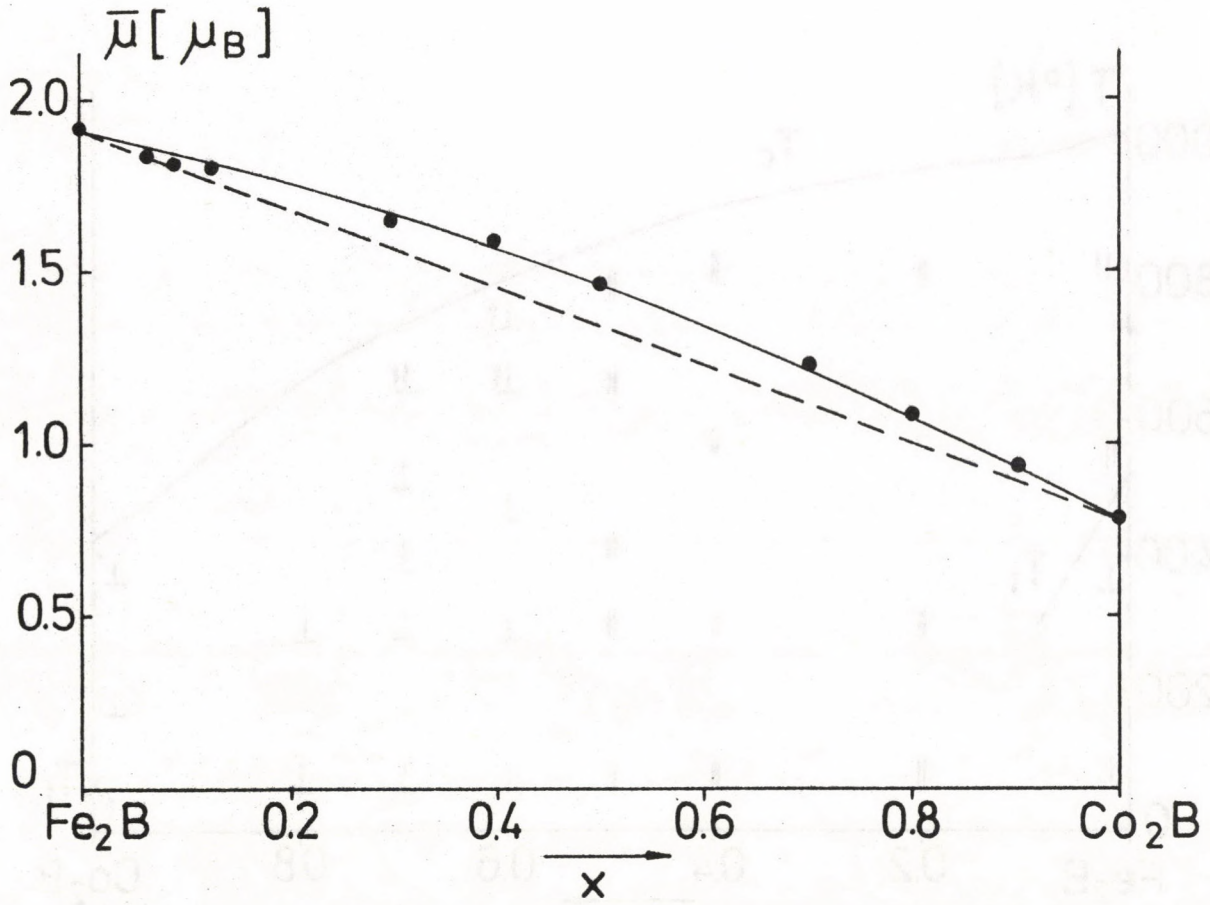


Fig. 4

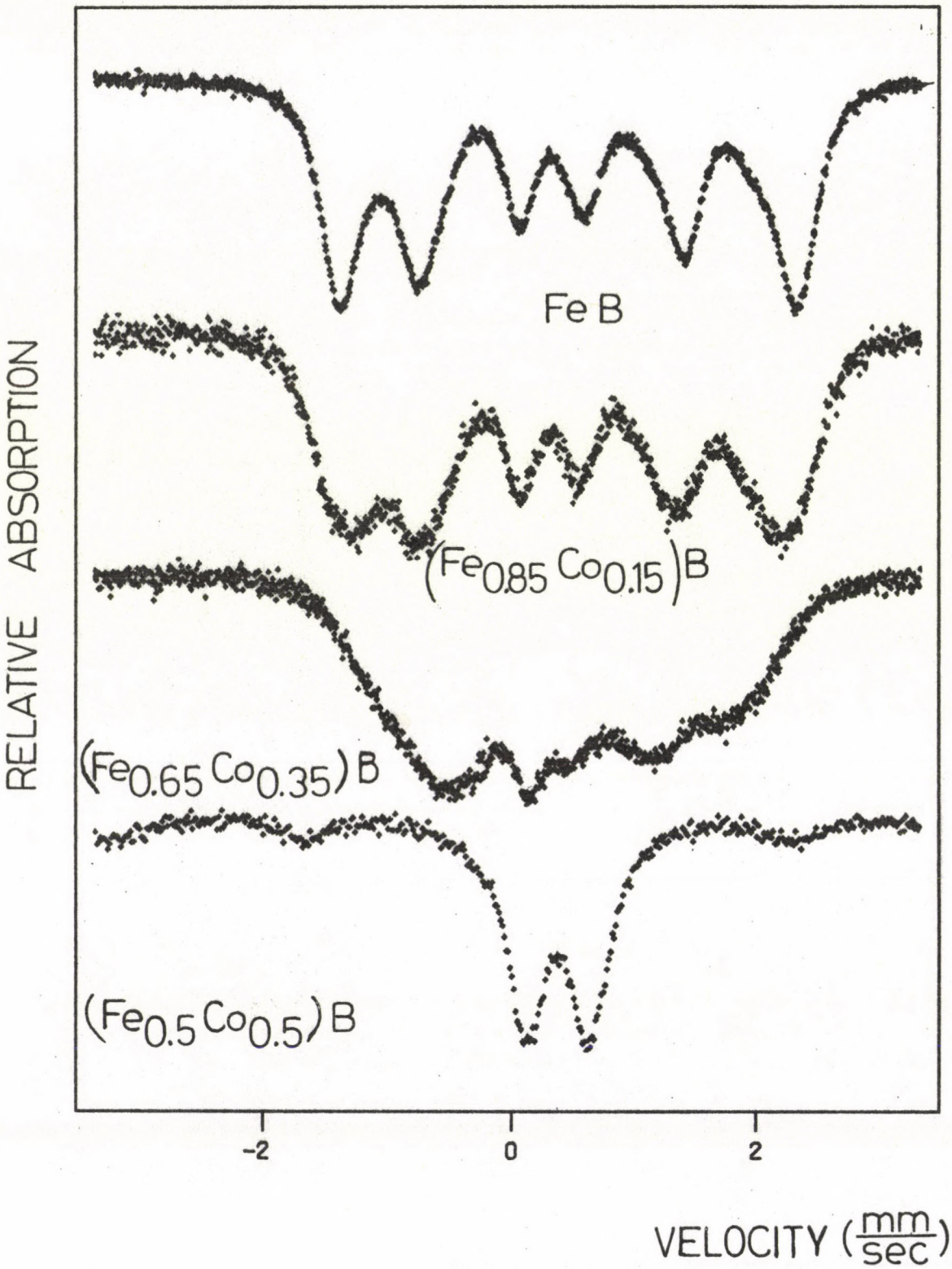
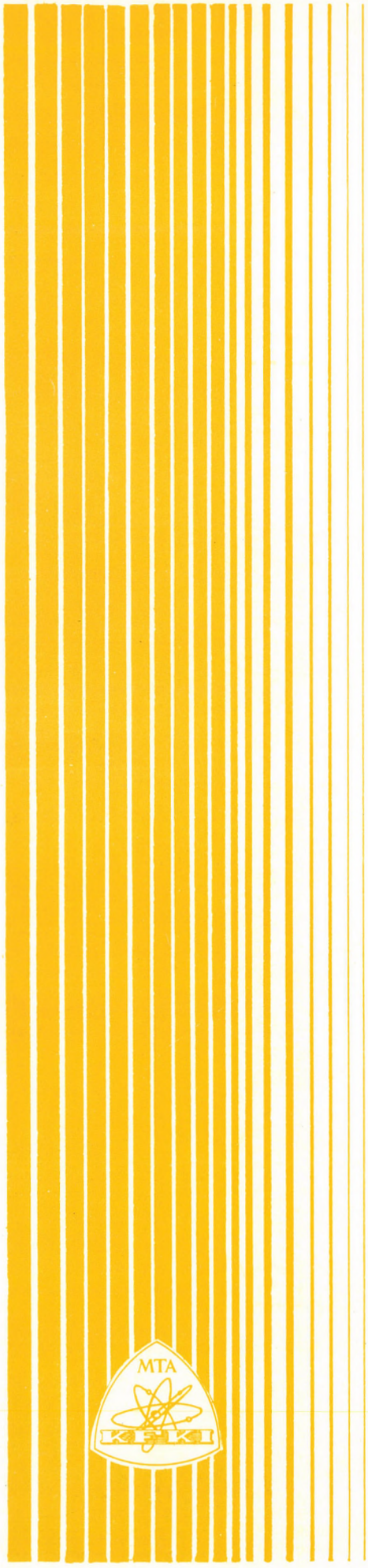

RELATIVE ABSORPTION
Fe B
(Fe0.85 Co0.15) B
(Fe0.65 Co0.35) B
(Fe0.5 Co0.5) B
-2
0
2
VELOCITY (mm/sec)

Fig. 5



Kiadja a Központi Fizikai Kutató Intézet
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