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HYPERFINE FIELD AND MAGNETIC MOMENTS IN bcc Fe-Co AND Fe-Ni

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ABSTRACT

The results of Mössbauer measurements on disordered bcc Fe-Co and Fe-Ni alloys are presented and it is shown that in these alloys the frequently used phenomenological expression $H_{Fe} = a\mu_{Fe} + b\mu$ gives a very poor description because of the tendency to short-range ordering. A simple explanation is given for the surprising decrease in the iron hyperfine field in contrast with the increase in the magnetic moment during the ordering in equiatomic FeCo by attributing the anomaly to the changes in the local neighbourhood of Fe atoms. The isomer shift data are compared with the increase in the number of iron d-electrons predicted recently by Hasegawa and Kanamori who used a single band tight binding CPA model and the experimental values show a reasonable agreement with the prediction.

РЕЗЮМЕ

Даются результаты мессбауэровских измерений, проведенных на неупорядоченных сплавах о.ц.к. Fe-Co и Fe-Ni. Показано, что вследствие их склонности к образованию ближнего порядка, часто применяемое феноменологическое выражение $H_{Fe} = a\mu_{Fe} + b\mu$ дает для них плохое описание. Необычное уменьшение сверхтонкого поля железа, обратное увеличению магнитного момента под влиянием упорядочения в эквиатомном сплаве Fe-Co, довольно просто объясняется изменением ближайшего окружения атомов железа. Данные изомерного сдвига сопоставляются с увеличением количества d-электронов, предсказанным в результате расчетов, проведенных Hasegawa и Kanamori. Экспериментальные значения находятся в рациональном соответствии в расчетными.

KIVONAT

Rendezetlen tck Fe-Co és Fe-Ni ötvözeteken végzett Mössbauer-mérések eredményeit közöljük, és megmutatjuk, hogy a gyakran használt $H_{Fe} = a\mu_{Fe} + b\mu$ fenomenologikus kifejezés ezekben az ötvözetekben nagyon rossz leírást ad a rövidtávu rend képzésére való hajlam miatt. Az ekviatomos Fe-Co-ban a rendeződés hatására a mágneses momentum növekedésével ellentétes meglepő csökkenést a vas hiperfinom terében egyszerű módon magyarázzuk a vasatomok lokális környezetének megváltozásával. Az izomereltolódás- adatokat összehasonlítjuk az ujabban Hasegawa és Kanamori végezte számítások által jóslott vas d-elektron-szám növekedéssel, és a kísérleti értékek ésszerű egyezésben vannak a számítottakkal.

The magnetic properties of disordered alloys of the 3d-transition metals have been subjects of interest for many years. Perhaps the most interesting problem is the spatial distribution of the magnetic moments in these alloys. For the direct determination of the magnetic moment distributions neutron scattering measurements are used. However, the accuracy of the available experimental values of the magnetic moments on the alloy components is poor being not better than 5-10%. The hyperfine fields measured by nuclear magnetic resonance method or by Mössbauer technique furnish information about both the 3d atomic moments and the conduction electron polarization in these alloys. Thus a firmly established relation between the atomic moments and the hyperfine field could give another possibility of determining the magnetic moments in alloys. To describe the hyperfine fields at the sites of both the hosts and the solutes one uses frequently the phenomenological expression

$$\bar{H}_A = a\bar{\mu}_A + b\bar{\mu} \quad , \quad (1)$$

where \bar{H}_A is the average hyperfine field at the nucleus of atom A in the alloy, $\bar{\mu}_A$ is the average moment of atom A, $\bar{\mu}$ is the average magnetic moment of the alloy and a and b are proportionality constants to be determined empirically. This relation reproduced approximately the hyperfine fields observed in a series of alloys as Ni-Co^{1,2}, Ni-Mn^{3,4}, Ni-Fe⁵, hexagonal Co-Fe² etc., however, the values of a and b are rather uncertain (e.g. $a_{Ni} = 20 \text{ kOe } \mu_B^{-1}$ was found in Ni-Fe⁵ while $a_{Ni} = 85 \text{ kOe } \mu_B^{-1}$ in Ni-Co¹). Part of the discrepancies arises from the large experimental error of the measured hyperfine fields and magnetic moments. Moreover, both of the

coefficients a and b may be affected by a change in the crystal structure (fcc or hexagonal).

One of the aims of the now reported Mössbauer measurements on the disordered bcc Fe-Ni and Fe-Co alloys was to investigate the relation between the magnetic moments and the iron hyperfine field. A previous study of dilute iron based alloys with transition metals has shown⁶ that the total change of the iron hyperfine field $\frac{d\bar{H}}{dc}_{Fe}$ is well described by the equation

$$\frac{d\bar{H}}{dc}_{Fe} = A\left(\frac{d\bar{\mu}}{dc} + \mu_{Fe} - \mu_i\right) + B(\mu_i - \mu_{Fe}) \quad (2)$$

where μ_i and μ_{Fe} are the magnetic moments of impurity and pure iron atoms, respectively. Here the a priori estimates of A and B are $150 \text{ kOe } \mu_B^{-1}$ and $80 \text{ kOe } \mu_B^{-1}$, respectively.

Equation 2 is the consequence of a simple model in which the conduction electron polarization has a linear response to the changes in d moment induced by the impurity. It is easy to see that equations 1 and 2 coincide in the dilute alloy case ($c \rightarrow 0$), when $a = A - B = 70 \text{ kOe } \mu_B^{-1}$ and $b = B = 80 \text{ kOe } \mu_B^{-1}$. We will compare the measured iron hyperfine fields in the above mentioned alloys with the equation

$$\bar{H}_{Fe} = a\bar{\mu}_{Fe} + b\bar{\mu} \quad (3)$$

using the parameter values $70 \text{ kOe } \mu_B^{-1}$ and $80 \text{ kOe } \mu_B^{-1}$ to investigate the validity range of this relation.

These investigations were stimulated in addition by the recent calculation of the electronic structure in these alloys performed by Hasegawa and Kanamori⁷ using coherent potential approximation to obtain a relatively simple and consistent model of these alloys. One result of this work is the evaluation of the average number of d-electrons for each

constituent atom. The thus calculated change in the number of iron d-electrons Δn_{Fe} relatively to those of pure iron can be directly compared with the observed isomer shift change if the number of 4s-electrons is unchanged as assumed in the calculation (using a tight-binding single band model). In the earlier Mössbauer investigation⁸ the change in the isomer shift of these systems proved to be of the same order of magnitude as the experimental error (i.e. $0.05 \frac{mm}{sec}$), thus a more accurate measurement was necessary.

A conventional constant-acceleration Mössbauer spectrometer was used with a 1024-channel analyser and a 20 mCi ^{57}Co in chromium source. Each spectrum was taken with $300-500 \times 10^3$ counts per channel, and the depth of the outer lines in the spectra was about $40-60 \times 10^3$ counts per channel.

Most of the alloys were prepared from at least 3N pure metals by induction melting under pure argon atmosphere. (Two Fe-Ni alloys (with 8 and 16 at.% Ni) were the same as those used in the average magnetization measurements³ and they were prepared by arc melting). After melting, the ingots were annealed for 10 h at $1000^\circ C$ in vacuum, then rolled to plates of 20-30 μm thickness, except two Fe-Co alloys (with 40 and 50 at.% Co) from which powder specimens with a grain size $< 50 \mu m$ were filed to attain the disordered phase. The ordered phase in these latter alloys was obtained by annealing at $850^\circ C$ for 20 h and then furnace-cooling to room temperature in one day. Since the weight losses on melting were negligible, the nominal compositions of all the alloys were assumed to be correct. The concentrations of

the samples were the following: Fe-Co: with 1.5, 3.0, 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 at.% Co; Fe-Ni: with 1.5, 3.0, 5.0, 8.0, 10.0, 13.0, 16.0, 20.0 and 25.0 at.% Ni.

There is no resolvable satellite in the Mössbauer spectra of these alloys and the change of the iron hyperfine fields due to the Co or Ni neighbours is manifested only by a broadening of linewidth. Due to this fact the least-squares fit of a single six-line pattern consisting of Lorentzian lines gives a satisfactory description of the spectra. The values of the average hyperfine field and the average isomer shift obtained from such a fit are shown in figures 1 and 2. Figure 1 shows also the results of the earlier Mössbauer measurements of deMayo et al.¹⁰, which were obtained with similar evaluation technique. The linewidth as a function of composition increases faster for Fe-Ni than for Fe-Co alloys, the increment is about 50 per cent with respect to pure iron both for 25 at.% Ni and 50 at.% Co substitution. On the other hand, the linewidth in the ordered Fe-Co (50 at.%) sample was the same as in pure iron.

The neutron scattering measurement of Collins and Forsyth¹¹ on ordered Fe-Co alloys has shown that the cobalt moment remains essentially constant while the moment on iron atoms increases with increasing cobalt concentrations. If the cobalt moment has about the same value ($1.80 \mu_B$) in the entire range of concentrations, the concentration dependence of the average iron moment $\bar{\mu}_{Fe}$ can be obtained

directly from the average magnetization data. Curve 2 in figure 3a shows the values of $\bar{\mu}_{Fe}$ obtained in this way in good agreement with the neutron data. On the other hand, curve 1 in this figure shows the values of $\bar{\mu}_{Fe}$ calculated from eq. 3 with $a = 70 \text{ kOe } \mu_B^{-1}$ and $b = 80 \text{ kOe } \mu_B^{-1}$ using the average hyperfine field data of figure 1. The two curves deviate substantially from each other and the discrepancy cannot be remedied by use of another set of a and b parameters. For example, a change of 50% in the only free parameter does not result in a significant change of the calculated $\bar{\mu}_{Fe}$. The large discrepancy between the two $\bar{\mu}_{Fe}$ curves can be seen from the solid line in figure 1 calculated for \bar{H}_{Fe} using the above mentioned a and b values and the curve 2 for $\bar{\mu}_{Fe}$ in figure 3a. The $\bar{\mu}_{Fe}$ curve obtained from the average magnetization data can be reproduced from the average hyperfine field data by assuming a decrease in the value of either a or b as a function of Co concentration. For example, curve 2 in figure 3a, shows $\bar{\mu}_{Fe}$ calculated from the hyperfine field data with the assumption that the b parameter depends linearly on the Co concentration, i.e. $b = (80 - 33 c_{Co}) \text{ kOe } \mu_B^{-1}$.

The relation between the iron hyperfine field and magnetic moments in Fe-Co obtained from experiments as

$$\bar{H}_{Fe} = a \bar{\mu}_{Fe} + b_0 \bar{\mu} (1 - k c_{Co}) \quad (4)$$

(with $b_0 = 80 \text{ kOe } \mu_B^{-1}$ and $k = 0.41$) could have the following simple explanation. Recent ^{59}Co NMR measurements¹² in dilute Fe-Co alloys (2 at.% Co) confirm that the Co atoms do not fill randomly the lattice, since Co avoids to have Co first neighbours. Thus, a considerable short-range order is expected in these „random“ alloys: the first neighbourhood of

iron will be dominated by Co atoms. In this case eq. 3 assumed to be valid for disordered alloys transforms up to 50 at.% Co to eq. 4. In this equation $k = \frac{\bar{\mu}_{Fe} - \mu_{Co}}{\bar{\mu}}$ arises from the concept of a B2-type short-range order and its value ranges from 0.27 to 0.48. The hyperfine fields calculated from eq. 4 with no adjustable parameters agree within 5 kOe of the measured values.

Another explanation of the concentration dependence of b could be the decrease in the number of conduction electrons. However, the isomer shift data do not allow any larger value than 0.1 for k and the concentration dependence of the isomer shift shows a saturation behaviour instead of the required linear increase above 20 at.% Co.

Very similar inferences can be made from the data on the Fe-Ni alloys, although the discrepancy is not so remarkable here as on Fe-Co because of the smaller concentration range and the very large uncertainty of the neutron scattering measurement. The $\bar{\mu}_{Fe}$ values obtained⁹ from the analysis of average magnetization data in ternary bcc Fe-Ni-Al alloys is thought to be the best approximation. The present $\bar{\mu}_{Fe}$ values obtained from the hyperfine field data are significantly different from this curve (figure 3b). The smaller deviation than in Fe-Co seems to be caused by a very weak Ni-Ni repulsion.

The surprising fact, that in Fe-Co the iron hyperfine field decreases during ordering while the average magnetization of these alloys increases, can be explained as follows. At the equiatomic composition the decrease in the hyperfine field is $\Delta H = \bar{H}_{Fe}^{disord} - \bar{H}_{Fe}^{ord} = 8 \text{ kOe}$. It is assumed that

the iron moment increases by $0.14 \mu_B$ for ordering¹³ - this affects ΔH in the opposite direction and contributes about -10 kOe to the above difference. However, the change in the local neighbourhood compensates this decrease. The substitution of the first Fe neighbours (on average four) by Co atoms due to the ordering results in a positive contribution to ΔH . This contribution can be estimated as about $4x \Delta H_1 = 4x8 = +32$ kOe, taking $\Delta H_1 = -8$ kOe due to the substitution of a first neighbour iron by cobalt (obtained from the decrease in the average hyperfine field ($\frac{d\bar{H}}{dc}Fe = -70$ kOe) between 30 and 70 at.% Co). The sum of these two contributions to ΔH is +22 kOe, which is further lowered by the changes in the second and third configuration sphere, the contributions of which are assumed to be proportional to $(\bar{\mu} - \bar{\mu}_{Fe})$. For example, if the change in the iron hyperfine field in the disordered phase caused by a second neighbour Co is about the half of ΔH_1 (and this does not seem to be too unrealistic)⁶, then we obtain exactly the observed value of ΔH . Thus it is not necessary to assume competing contributions to the hyperfine field as it was done by deMayo et al.¹⁰ for the explanation of the concentration and ordering dependence of the iron hyperfine field in Fe-Co.

It seems that there are serious problems in using eq. 1 to describe the concentration dependence of the hyperfine fields in a wide concentration range. The discrepancy generally is non-apparent when the magnetic moments are unchanged and the hyperfine field has a linear concentration dependence (e.g. Ni-Co) or because of the very limited accuracy of both the reported hyperfine field and neutron

scattering measurements.

According to the recent single band tight binding CPA calculation of Hasegawa and Kanamori⁷, the number of d-electrons at iron atoms increases relative to pure iron with impurity concentration in both alloys. Assuming that the 4s-electron density is unchanged we can directly compare the results of this calculation with the measured change in the isomer shift (the increase in the 3d-electron number reduces the 3s-electron density at the nucleus and thus results in an increase of the isomer shift). Although the value of the proportionality constant is questionable within a factor of two¹⁴ and could be different for the two systems, the two calculated curves in figure 2 show the same tendency as the measured points.

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Figure Captions

- Figure 1a. Concentration dependence of the average hyperfine field at iron sites in Fe-Co both in the disordered and ordered phase. The figure contains also the results of the earlier measurement of deMayo et al.¹⁰. The curve is calculated from eq. 3 using the values $a = 70 \text{ kOe } \mu_B^{-1}$ and $b = 80 \text{ kOe } \mu_B^{-1}$, and $\bar{\mu}_{\text{Fe}}$ as obtained from the average magnetization data assuming that $\mu_{\text{Co}} = 1.80 \mu_B$ is constant in the whole concentration range (curve 2 in figure 3a).
- Figure 1b. Concentration dependence of the average hyperfine field at iron sites in Fe-Ni at room temperature and liquid nitrogen temperature.
- Figure 2. The change of the isomer shift at iron sites in Fe-Co and Fe-Ni as a function of concentration. The increase in the number of iron d-electrons Δn_{Fe} calculated by Hasegawa and Kanamori⁷ is shown as well.
- Figure 3. Concentration dependence of the average iron moment $\bar{\mu}_{\text{Fe}}$ in Fe-Co calculated from the average hyperfine field using eq. 3 with $a = 70 \text{ kOe } \mu_B^{-1}$ and $b = 80 \text{ kOe } \mu_B^{-1}$ (curve 1, dotted line) or with $a = 70 \text{ kOe } \mu_B^{-1}$ and $b = (80 - 33 c_{\text{Co}}) \text{ kOe } \mu_B^{-1}$ (curve 2, dot-dashed line). This latter curve coincides with that obtained from the average magnetization assuming that $\mu_{\text{Co}} = 1.80 \mu_B$ is constant in the whole concentration range. The average magnetization¹³ and the iron moment obtained in

ordered alloys by neutron scattering¹¹ are shown as well.

Figure 3b. Concentration dependence of the average iron moment $\bar{\mu}_{\text{Fe}}$ in Fe-Ni calculated from the average hyperfine field at 80 °K using eq. 3 with $a = 70 \text{ kOe} \mu_{\text{B}}^{-1}$ and $b = 80 \text{ kOe} \mu_{\text{B}}^{-1}$ (curve 1, dotted line) and that obtained⁹ from the evaluation of average magnetization data in ternary Fe-Ni-Al alloys (curve 2, dot-dashed line). The average magnetization⁹ and the result of the neutron scattering experiment¹¹ are shown as well.

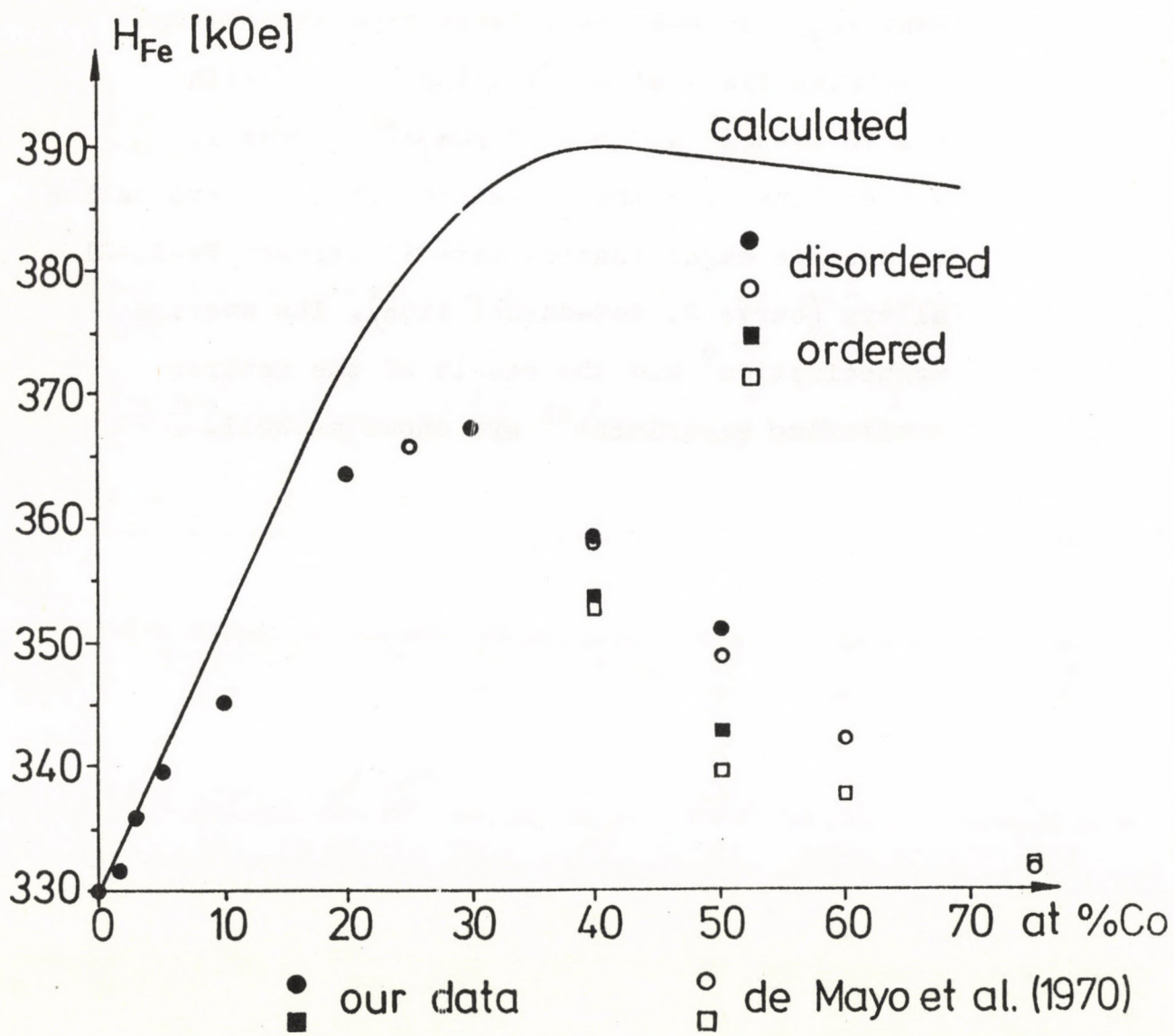


Fig. 1

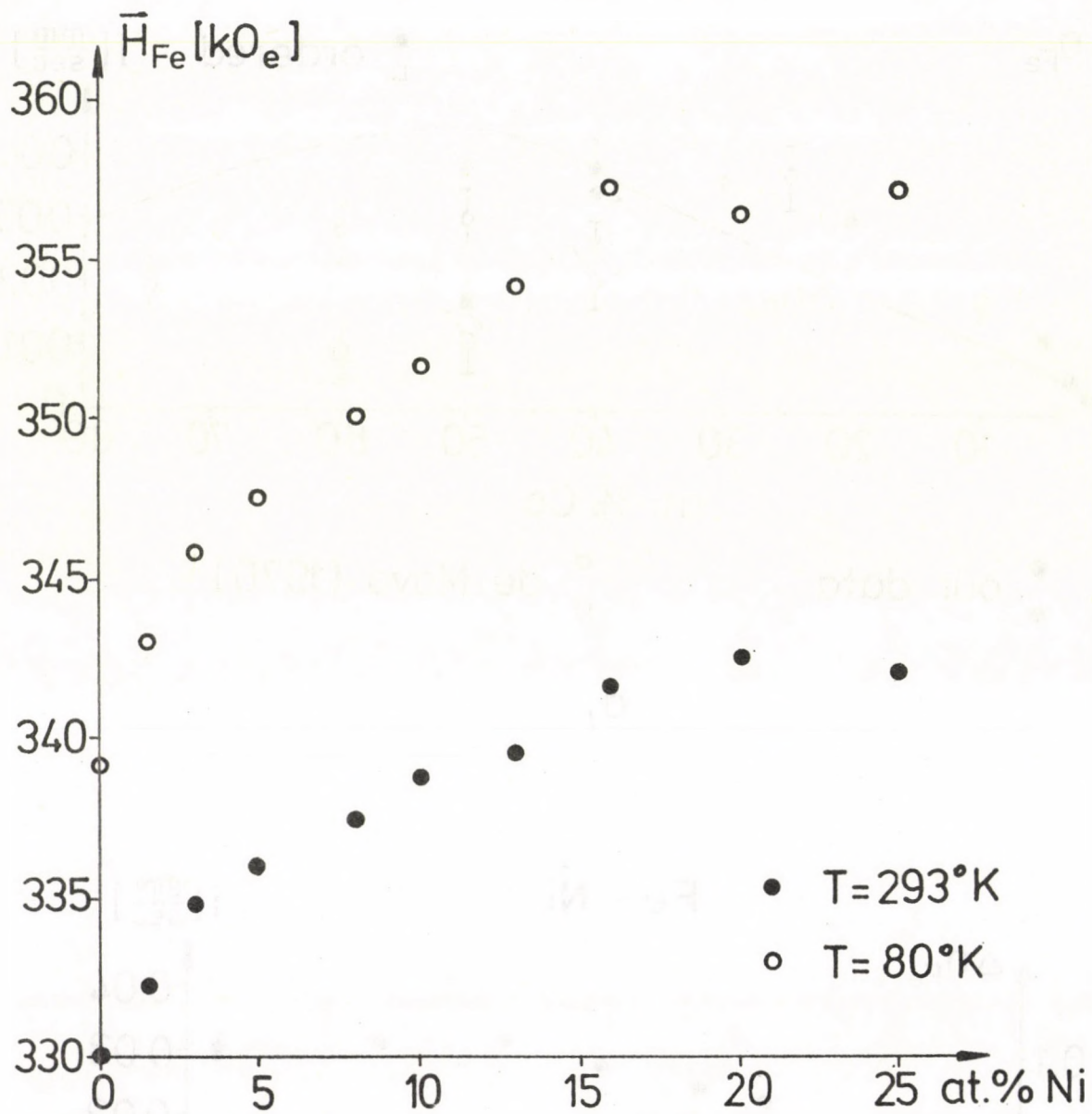
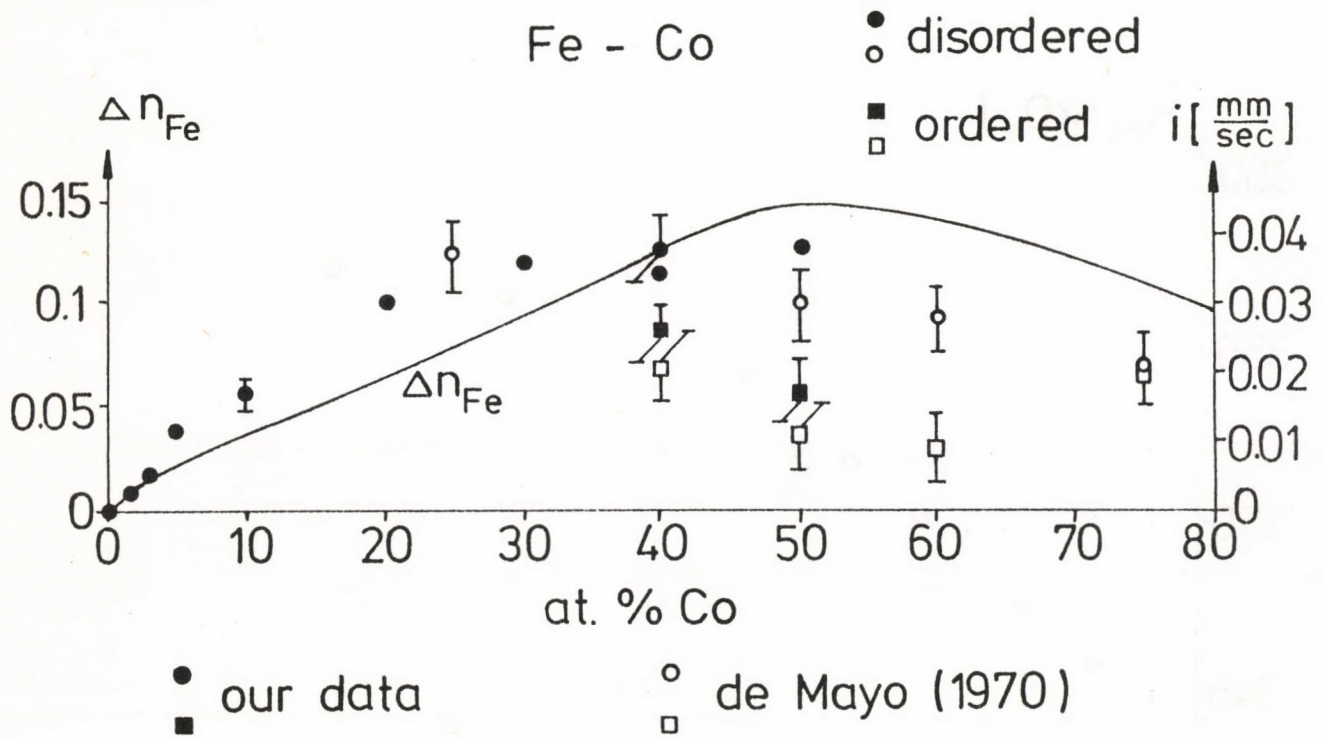
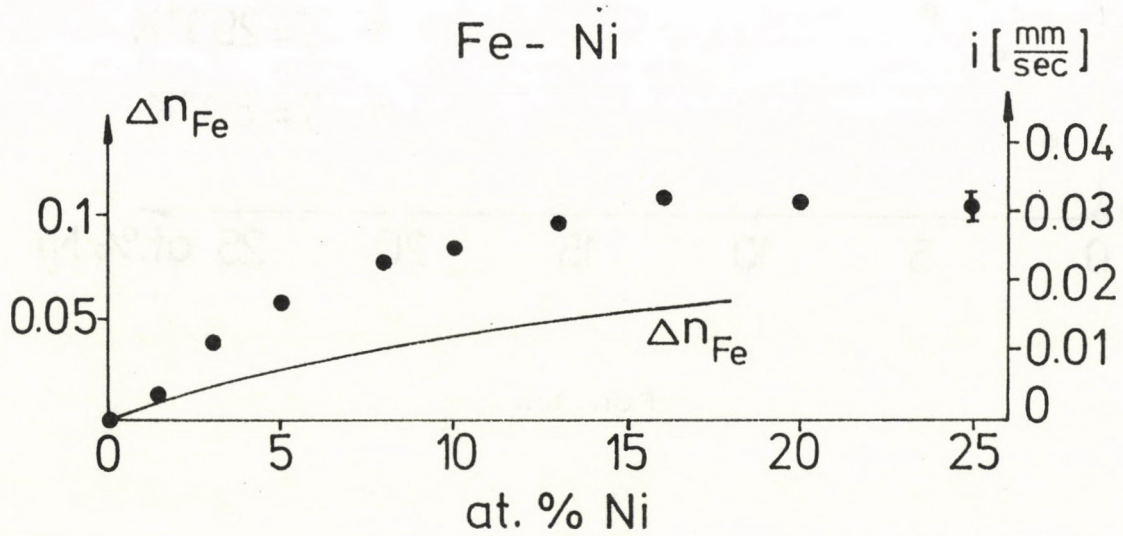


Fig. 1/b



a,



b,

Fig. 2

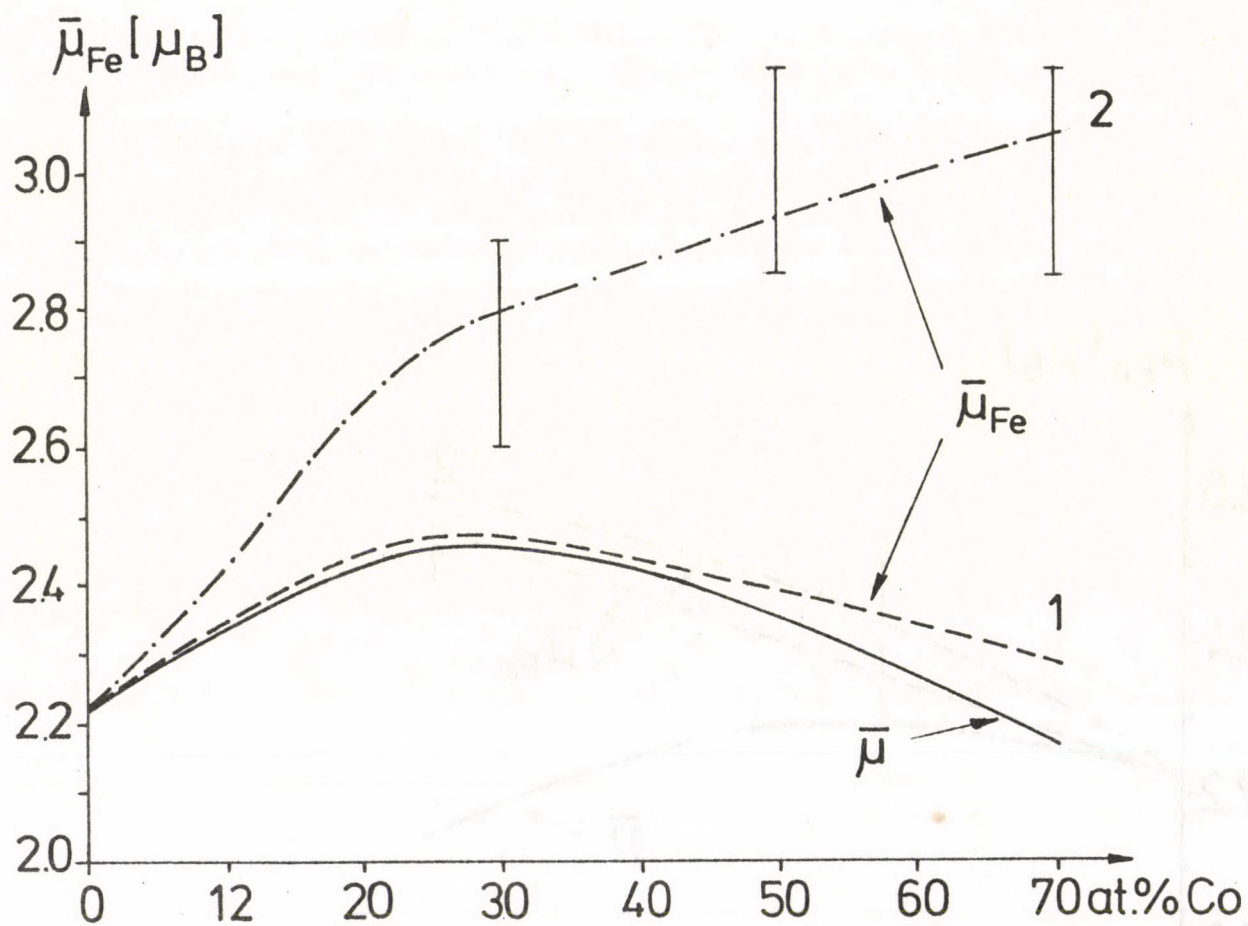


Fig. 3/a

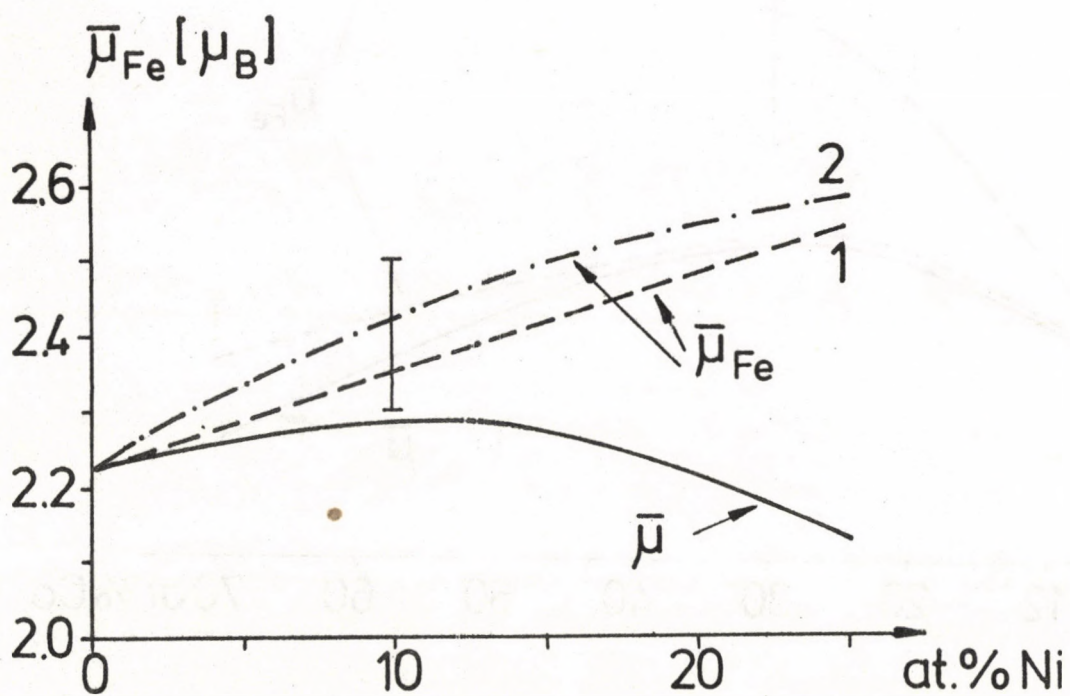
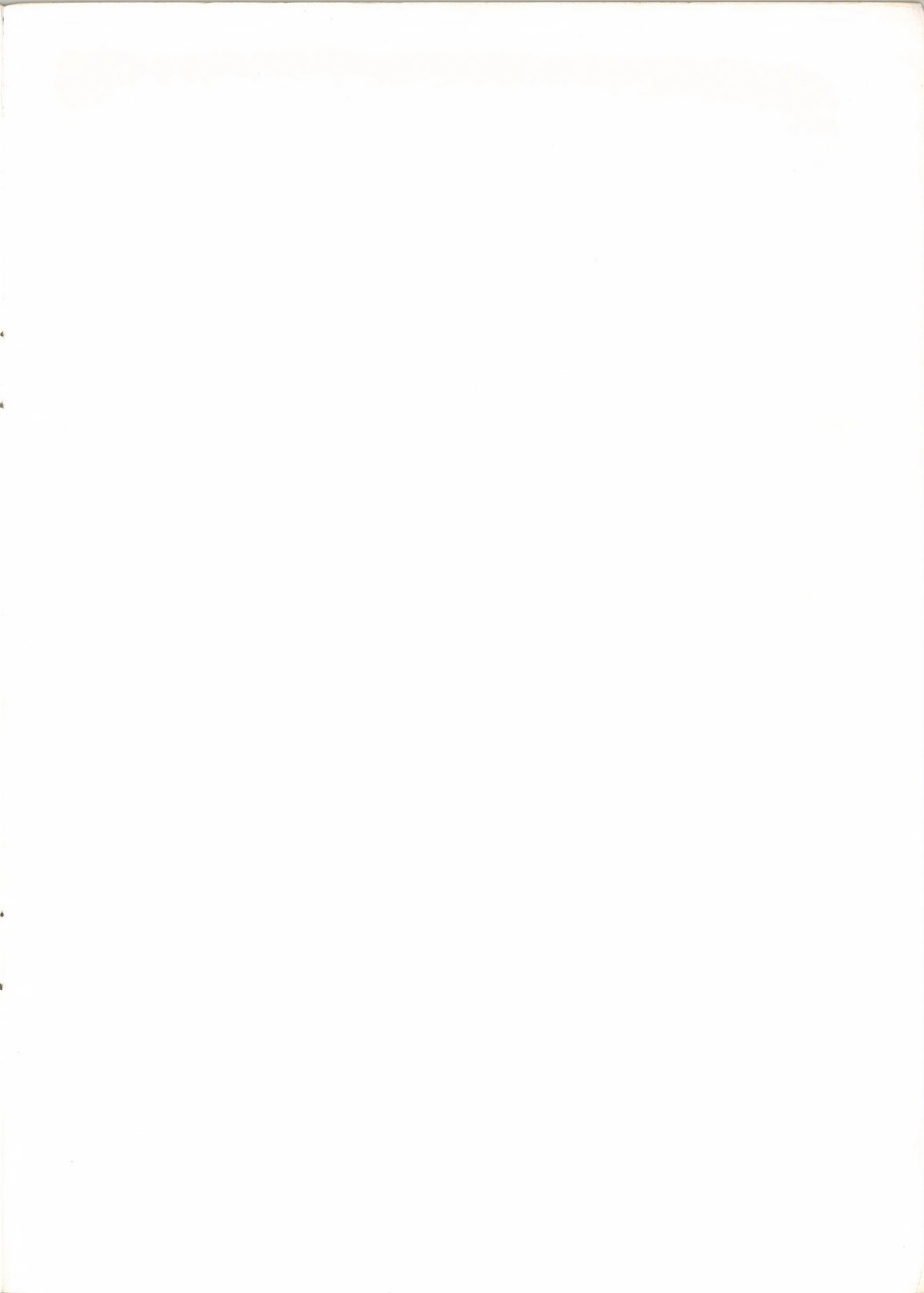


Fig. 3/b



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