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KÖZPONTI FIZIKAI KÖNYVTÁRA BUDAPEST

G. Grüner
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^{27}Al NMR SPECTRA IN Al-3d TRANSITION METAL ALLOYS

G. Grüner, K. Tompa

Central Research Institute for Physics, Budapest, Hungary
Solid State Physics Department

and

E. Kovács-Csetényi, C.R. Vassel

Research Institute for Non-Ferrous Metals, Budapest, Hungary

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ABSTRACT

The electric and magnetic perturbations around Mn, Cr and Fe impurities in aluminium were investigated by measuring the ^{27}Al NMR spectra of these alloys. The first order quadrupole wipe-out numbers measured at low impurity concentrations, and the magnetic field dependence of the signal amplitude in more concentrated alloys are discussed in the framework of the Friedel-Anderson picture.

KIVONAT

A Mn, Cr és Fe szennyezések körüli perturbációt vizsgáltuk aluminiumban a ^{27}Al MNR mérésével. A kis koncentrációju mintákban mért elsőrendü kvadrupol effektust, és a jelamplitudó mágneses tér függését a nagy koncentrációju mintákban értelmeztük a Friedel-Anderson kép alapján.

РЕЗЮМЕ

Был измерен спектр ЯМР ^{27}Al для исследования электронных и магнитных возмущений в окрестности примесей Mn, Cr и Fe алюминиевых сплавов. На основе теории Фриделя-Андерсона рассматриваются число уничтожения квадрупольного эффекта первого порядка, измеренное при низкой концентрации примесей, а также зависимость магнитного поля от амплитуды сигнала в сплавах с более высокой концентрацией.

1. INTRODUCTION

The electronic structure of transition metal impurities in aluminium has been the subject of considerable theoretical and experimental work in recent years. The temperature dependence of the impurity resistivity [1] and the superconducting transition temperature, susceptibility and specific heat [2] can be interpreted well in the framework of the Anderson model, providing the transition metal impurities in aluminium are nearly magnetic and that the localised spin fluctuations are important [3][4].

The aim of our NMR measurements was the investigation of the local spin and charge perturbation around transition impurities by measuring the ^{27}Al resonance in dilute Al-Fe, Al-Mn and Al-Cr alloys. As it was shown, metallurgical problems /e.g. low solubility in aluminium/ have an important effect [5], and the NMR investigations on Al-Fe and Al-Mn alloys [6] cannot be regarded as confirmatory evidence of the simple Anderson picture. On the other hand, our measurements can be regarded as adding to the results of NARATH [7] and LAUNOIS [8], who measured the impurity Knight shift and relaxation time, and the perturbation on the nearest-neighbour matrix atoms.

2. EXPERIMENTAL DETAILS AND RESULTS

Zone-refined aluminium of nominal 99,999 % purity /Fe-Si-Cu content lower than 10 ppm/ was used for preparation of the alloys; transition element impurities were estimated to be less than 1 ppm. Specimens of desired composition were prepared by dilution of master alloys and analysed by spectrographic analysis /Al-Fe alloys/ or by potentiometric titration /Al-Mn and Al-Cr alloys/. The samples were cold rolled to about 20 μ thickness to avoid skin effects, annealed for one hour at 600°C /low concentration alloys/ or at 630°C /higher concentration alloys/, and afterwards quenched in cold water. /Several other annealing temperatures were used for the Al-Mn alloys to investigate the effect of the annealing temperature./ Electrical resistivity was measured at 4.2°K, 77°K and room temperature. The change of the resistivity was proportional to the concentration, and the impurity resistivity measured at different temperatures is shown in Fig. 1, which includes our measurements on Al-Cu alloys too.

The NMR experiments were performed at room temperature in the H = 4-10 kG range, with a modulation amplitude H_m = 2G. Samples of nearly identical volume were taken and the ^{63}Cu signal from a copper foil was used as the marker. The signal-to-noise ratio was about 100. Asymmetry due to the skin effect was only slight so that it probably does not modify the results.

The concentration dependence of the amplitude /i.e. the peak-to--peak amplitude of the derivative signals/ measured on the alloys of low concentrations is shown in Fig. 2. Since the NMR data at low concentrations showed an anisotropy of a few percent, the values given are averages of spectra measured in different directions. It is worth mentioning that quenching from temperatures other than 600°C results in a slight change of the signal amplitude but leaves the slope of the concentration dependence unchanged. The amplitudes at low impurity concentrations were independent of the external magnetic field*.

The amplitudes measured on high concentration alloys at various external magnetic fields at room temperature are shown in Fig. 3. The line widths measured at different heights of the resonance signal showed a linear increase with increasing magnetic field.

3. DISCUSSION

The results obtained with the low and high concentration alloys will be discussed separately.

a/ Low concentration alloys

The dominant effect at low impurity concentrations is the reduction of the signal amplitude as a result of the first order quadrupole effect. According to the "all-or-nothing" model [9]

$$D/D_o = /1-c/^n \qquad /1/$$

where D and D_o are the satellite contributions to the signal amplitude of the alloy and of pure Al, respectively, and c is the impurity concentration. The "wipe-out number" characterizes the range of the perturbation, and is connected with the number of matrix atoms around an impurity, which experiences a field gradient greater than a critical value q_o.

*The results of [6] are in agreement with ours, taking into account that the wipe-out number is determined by the slope of the concentration dependence and that the effective impurity concentration is greatly reduced in Al-Fe due to precipitation processes [2] [5].

The electric field gradient q at solvent atom sites results from the redistribution of the conduction electron charge around the impurities [6]. At large distances from the impurities

$$q(r) = \frac{8\pi}{3} \beta\alpha \frac{\cos(2k_F r + \varphi)}{r^3} \qquad /2/$$

where the factor β depends on the properties of the matrix and for Al has a value of 23 [10], and where the oscillation amplitude α and the phase factor φ are determined by the phase shifts of the scattered conduction electrons at the Fermi surface. In the case of nonmagnetic transition metal impurities the $\ell = 2$ phase shift dominates, all the other phase shifts being small. In the FRIEDEL-ANDERSON picture $\eta_2 = \frac{N\pi}{10}$, where N is the number of electrons in the unfilled d shell of the impurity, and $\alpha = 5\sin\frac{N\pi}{10}$ and $\varphi = \frac{N\pi}{10}$ [6]. Going through the 3d-series one expects a maximum of the oscillation amplitude between Cr and Mn, with a smaller value in the case of Fe.

It can be shown that in a refined version of the "all-or-nothing" model the wipe-out number does not depend much on the phase factor φ and that the oscillation amplitude is proportional to the wipe-out number [11]. Fig. 4 contains the measured first order wipe-out numbers /determined from a logarithmic plot of the amplitudes normalized to the satellite contribution/ and the wipe-out numbers computed from the residual resistivity. The value of 1700 for Al-Fe corresponds to the effective impurity concentration determined by resistivity measurements; the value 1500 to the concentration determined by analysis [5]. The wipe-out numbers of Al-Cu measured by us, and that of Al-Zn [12] are also included. There is a good agreement between the measured and calculated values for Al-Fe, but there is a clear disagreement in the case of Al-Cr and Al-Mn. Though some metallurgical effects such as impurity-dislocation interaction or the effect of vacancies frozen in by quenching cannot be excluded, the disagreement finds its natural explanation in the temperature dependence of the density of the resonant d states [4] causing a change of the oscillation amplitude in the case of nearly magnetic impurities. A report on the temperature dependence of the oscillation amplitude and its relation to the LSF effects [4] will be published later [17].

b/ High concentration alloys

In the high concentration alloys the satellite contribution are nearly wiped out, and therefore the parameters of the spectra are determined by the second order quadrupole effect /proportional to H^{-1}/ and by magnetic perturbation /proportional to H/. The nearly linear decrease of the amplitude and the broadening of the spectrum show that the magnetic perturba-

tion, which is proportional to the impurity concentration and which is about 1,5 times as great in Al-Mn as in Al-Cr, dominates in this magnetic field range.

To a first order approximation there are two contributions proportional to the external magnetic field. Because of the enhancement of the impurity states the phase shifts of the spin up and spin down electrons differ, $\eta_2^{\uparrow} \neq \eta_2^{\downarrow}$. This difference of the perturbation in the two bands leads to a spin density disturbance around the impurity and a Knight-shift change [13] of

$$\frac{\Delta K}{K} = \frac{10}{4\pi^2} \frac{\Omega}{2N_o} \frac{\eta}{\Delta} \cos(2k_F r) \cdot r^{-3} \qquad /3/$$

where Ω is the volume of the unit cell, N_o the density of s states at the Fermi level for one spin direction, η the enhancement factor, Δ the width of the resonant state, and K the Knight shift. On the other hand, the charge distribution around the impurity yields the distribution of the Knight shift on the neighbouring atoms [14]:

$$\frac{\Delta K}{K} = \pm 5 \sin\eta_2 \sin(2k_F r + \varphi) \times (2k_F r)^{-2} . \qquad /4/$$

The first effect is proportional to the susceptibility localised on the impurity site, the second resembles the parameter $\sin\eta_2$ appearing in the impurity resistivity and the first order wipe-out number. /The different radial dependences of the two perturbations should be noted: at short distances from the impurity the first is greater and at longer ones the second./

The results in Fig.2 clearly show that the first effect dominates: the field dependence is roughly proportional to the susceptibility, which is about 1,5 times as great in Al-Mn as in Al-Cr, rather than to the residual resistivity or first order wipe-out number. To compare the results with the parameters determining the above two expressions some corrections have to be made. The amplitude extrapolated to $H = 0$ clearly shows that some residual satellite transitions adding a field-independent contribution to the resonance signal are present. Also a correction due to the field dependence of the second order quadrupole effect was estimated from the field dependence measured on high concentration Al-Zn alloys [16]. In the 5-10 kOe range this yields a positive contribution of about +6% to the normalized amplitude change. Taking into account these corrections $D^{-1}_{H\to O}\, dD/dH = -4{,}1.10^{-2}$ kG^{-1} is obtained for the highest concentration Al-Mn alloy.

The resonance line shapes at different magnetic field were computed as in [15], assuming the contributions /3/ and /4/. Using the parameters $\eta/\Delta = 12\ eV^{-1}$ determined from the susceptibility measurements [1] and $\eta_2 = \pi/2$, we get $D^{-1}_{H\to O}$, $dD/dH = 4{,}0.10^{-2}\ kG^{-1}$ for the Al-0,57% Mn alloy which agrees well with the measured value. Equally good agreement can be obtained with the susceptibility results in Al-Cr alloys.

Finally, we mention that the zero value of the first moment /average line shift/ indicates the absence of a negative definite, long-range spin polarization around Mn and Cr impurities in aluminium, and shows that the susceptibility is localised at the impurity site, in agreement with the observation of NARATH and WEAVER [7].

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FIGURE CAPTIONS

Fig. 1 Impurity resistivity of Al-Fe, Al-Mn, Al-Cr and Al-Cu alloys at different temperatures.

Fig. 2 Concentration dependence of the peak-to-peak amplitude of the ^{27}Al absorption derivative in Al-Fe, Al-Mn and Al-Cr alloys.

Fig. 3 Field dependence of the ^{27}Al absorption derivative in concentrated Al-Cr and Al-Mn alloys.

Fig. 4 Measured and calculated wipe-out numbers in Al-based alloys.

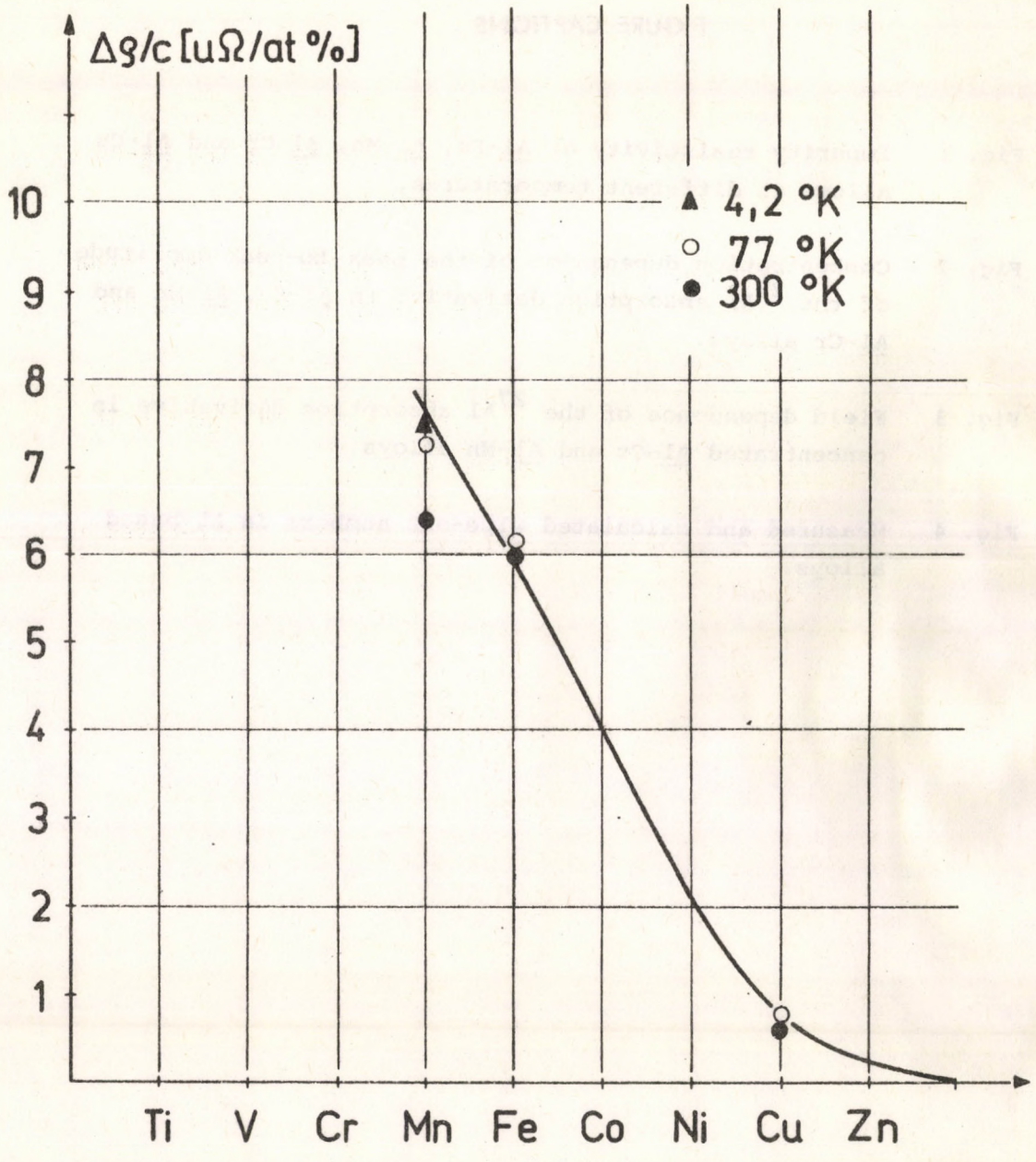


Fig. 1

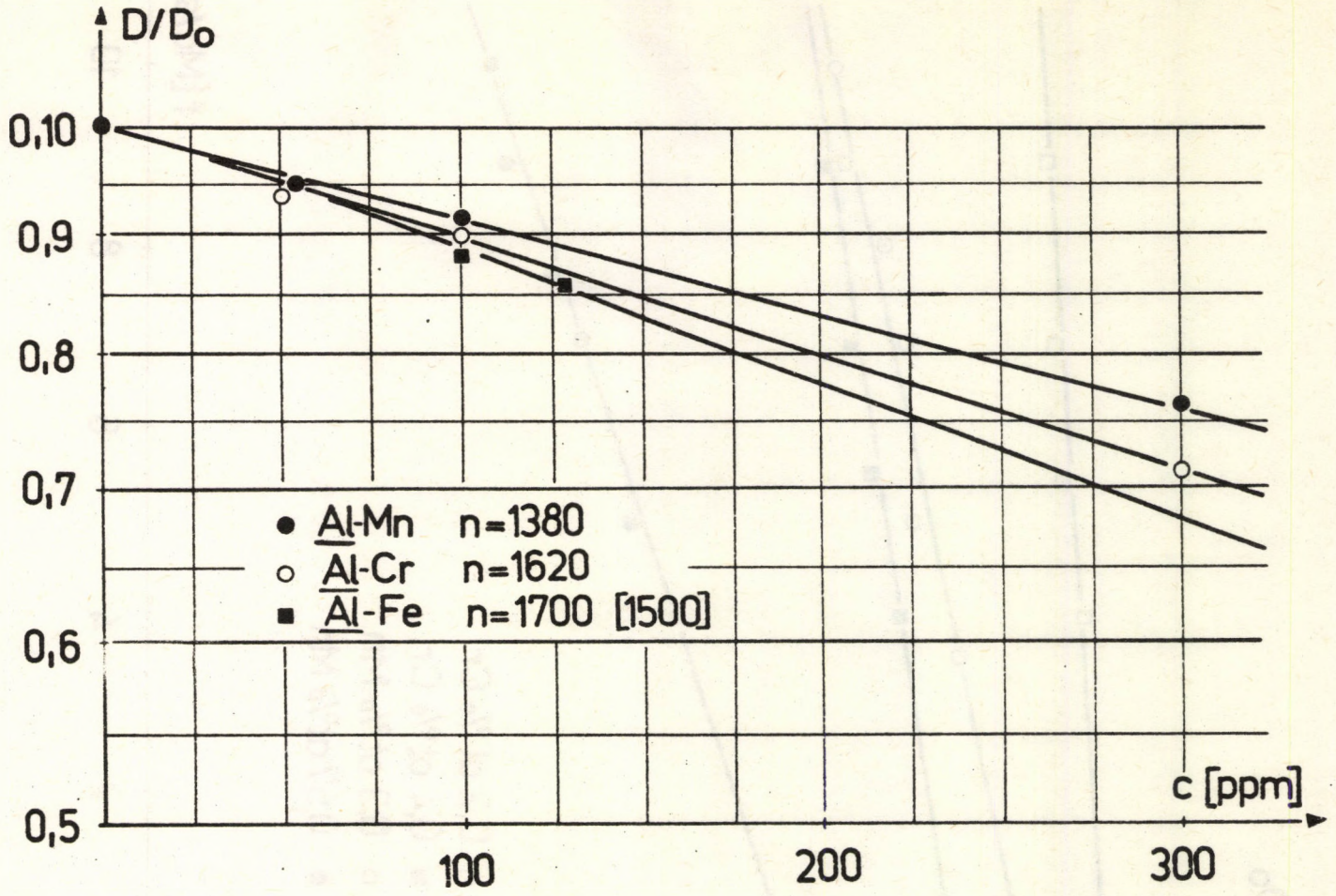

D/Do
0,10
0,9
0,8
0,7
0,6
0,5
100
200
300
c [ppm]
● Al-Mn n=1380
○ Al-Cr n=1620
■ Al-Fe n=1700 [1500]

Fig. 2

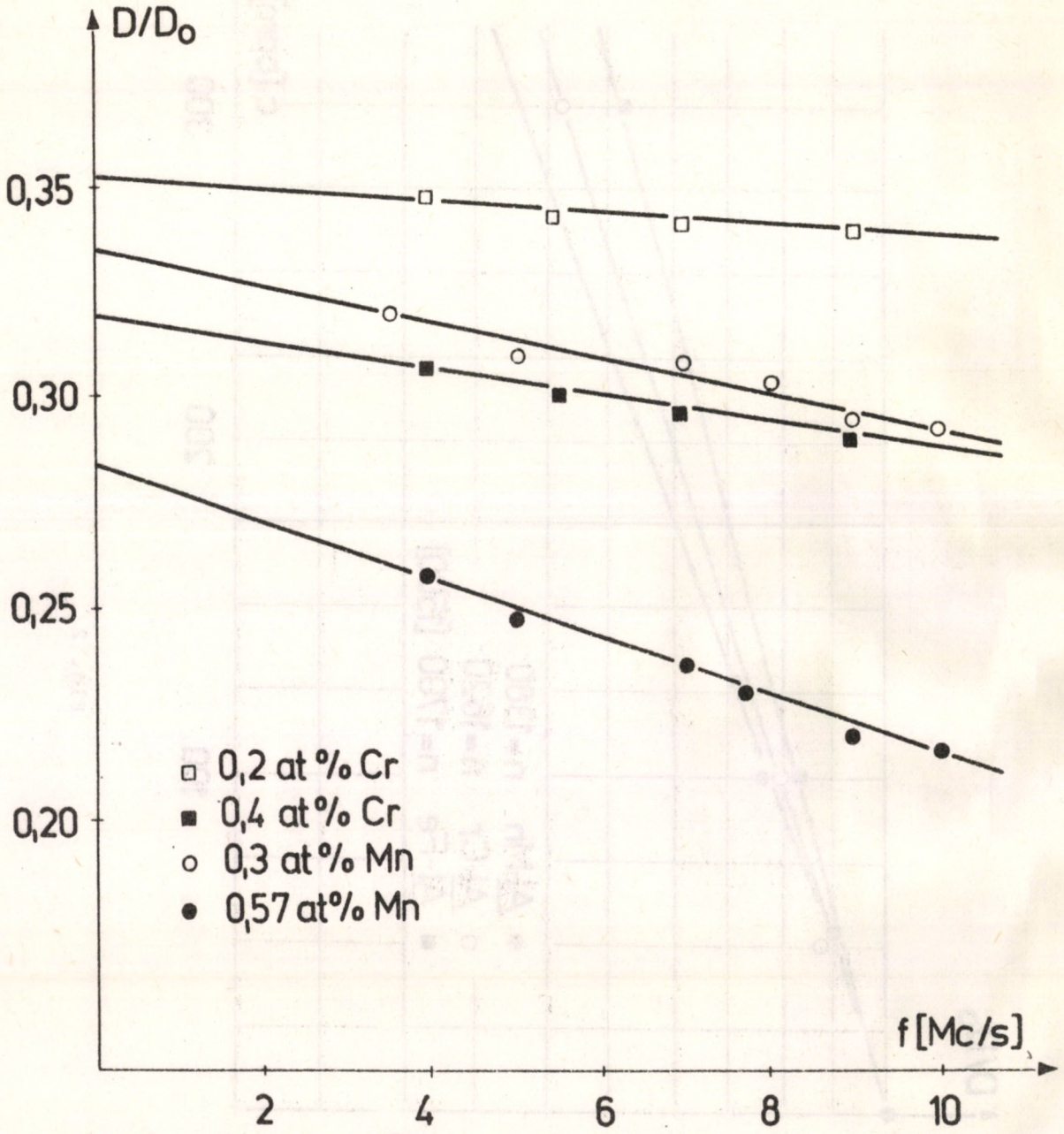

D/D₀
0,35
0,30
0,25
0,20
□ 0,2 at % Cr
■ 0,4 at % Cr
○ 0,3 at % Mn
● 0,57 at % Mn
f [Mc/s]
2
4
6
8
10

Fig. 3

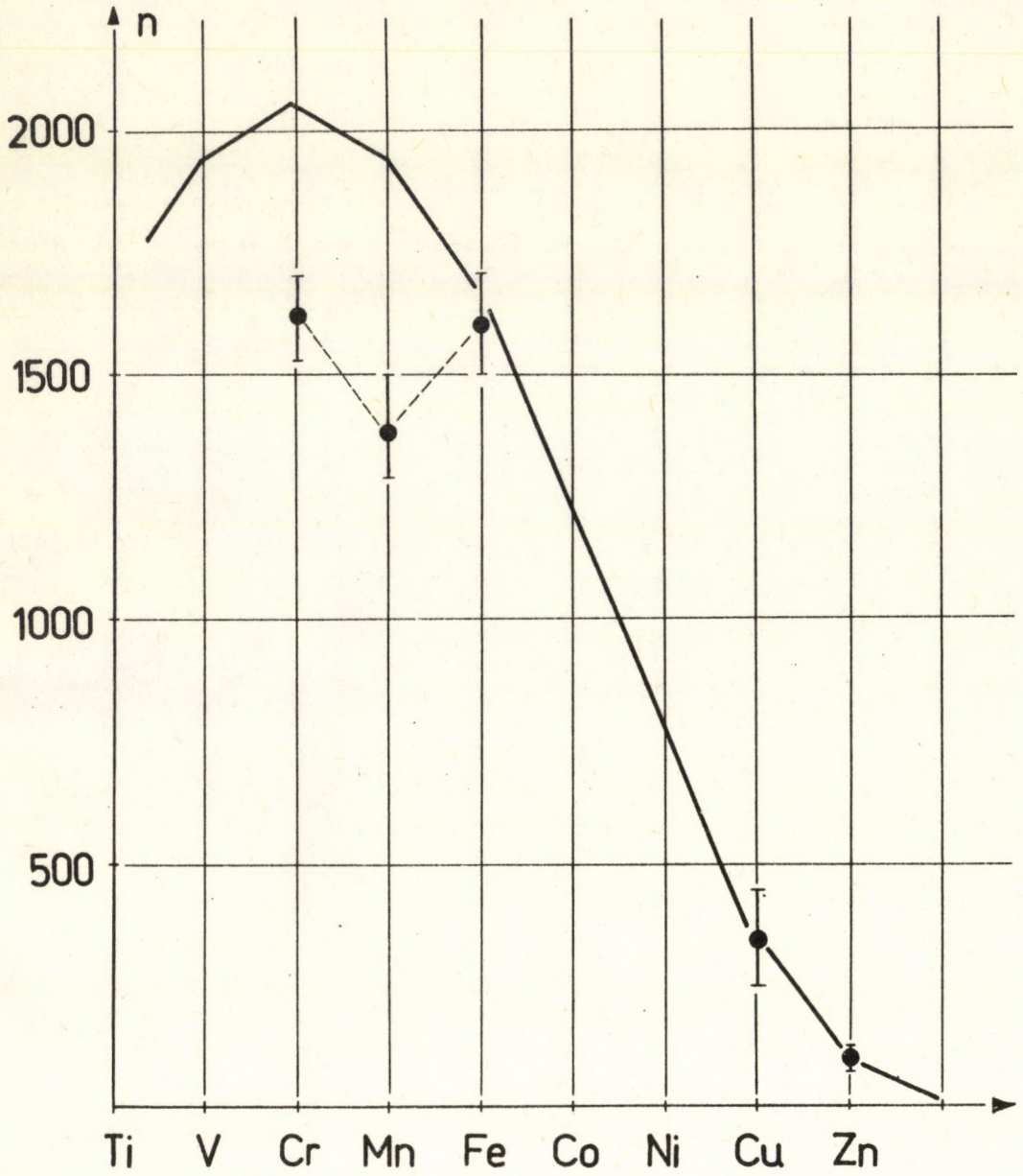
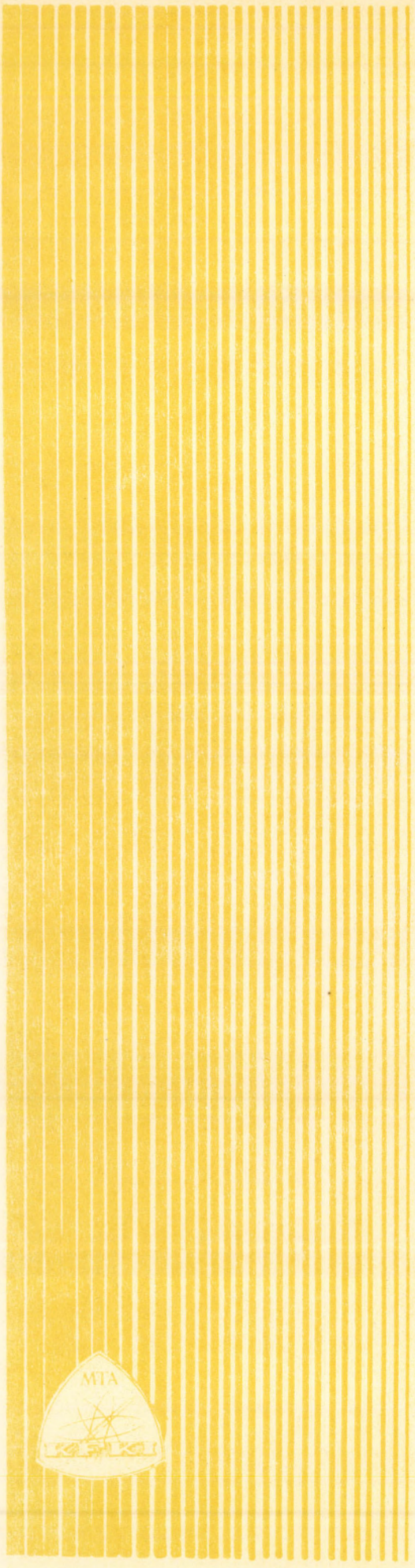


Fig. 4

61-870



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