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ABSTRACT

The second moment of the ^{27}Al NMR signal was measured at room temperature in pure Al and Al - 3d-transition metal alloys. The second moment of pure Al is a sensitive function of metallurgical effects such as cold rolling and quenching, while its concentration dependence as a function of impurity atomic number shows a double-peaked behaviour. Comparison of the line broadening with the amplitude reduction of the resonance signal suggests that no drastic preasymptotic effects occur in these alloys.

РЕЗЮМЕ

Измерения второго момента сигнала ЯМР на ядрах Al^{27} чистого алюминия и алюминиевой матрицы, содержащей примеси 3d-элементов переходной группы показали, что значение второго момента сильно зависит от способа холодной обработки и быстрого охлаждения образцов. Концентрационная зависимость второго момента имеет два максимума в функции атомного номера примеси. Сравнивая уширение сигналов при увеличении концентраций со спадом их амплитуд установили, что не было заметно значительных преасимптотических эффектов.

KIVONAT

Tiszta Al-ban és Al-3d-átmeneti fémötvözetekben mértük a ^{27}Al NMR jelének második momentumát szobahőmérsékleten. A tiszta Al második momentuma érzékenyen reagál a metallurgiai megmunkálás - hideghengerlés, gyorshütes - közben fellépő hatásokra. A második momentum koncentráció-függése kettős csucsot mutat a szennyező elem atomszámának függvényében. A vonalszélesedésnek a rezonanciajel amplitudó-csökkenésével való összehasonlitása arra utal, hogy ezekben az ötvözetekben nem volt megfigyelhető jelentős preaszimptotikus effektus.

INTRODUCTION

The virtual bound states of transition metal impurities in non-magnetic metal hosts give rise to two well-observable effects in the host matrix due the redistribution of the conduction electrons: namely, spin and charge density perturbations around the impurities. The charge density perturbation is normally attributed to the asymptotic form /Friedel, 1956/

$$\Delta\rho(r) = \alpha\cos(2k_F r + \varphi)/r^3 \qquad /1/$$

where the amplitude α and the phase φ of oscillation are dependent on the parameters of the virtual bound state and can be expressed by the phase shifts of the scattered conduction electrons.

This classical formula for the charge density oscillation around a scattering centre within an electron gas was derived by neglecting the energy dependence of the phase shifts $\delta_1(\omega)$ describing the scattering. In the case of d-transition metal impurities, however, the existence of the virtual bound state near to the Fermi level will result in a strongly energy-dependent d-type scattering, and hence in serious deviations from Friedel's simple formula at small distances r. According to the theory of the preasymptotic behaviour of the charge density oscillation around resonant scatterers recently worked out by Mezei and Grüner /1972/ the range of validity of the Friedel asymptotic formula is determined by the coherence length ξ_Δ. If $r \leq \xi_\Delta$, then $\Delta\delta(r)$ will change much slower than is given by the r^{-3} law, and as $r \to 0$ it will approach rather a r^{-2}.

In the case of a Lorentzian-shaped resonance the coherence length may be expressed as

$$\xi_\Delta = \frac{V_F}{2\Gamma} \qquad /2/$$

where V_F is the Fermi velocity of the conduction electrons and Γ is the half width of the scattering amplitude.

The electric field gradient, which interacts with the quadrupole moment of the host nuclei has the form:

$$\Delta q(r) = \frac{8\pi}{3} \mu \Delta(r) \qquad /3/$$

where μ is the antishielding factor /Kohn, Vosko 1960/. This interaction perturbs the Zeeman energy levels of the nuclei and causes a shift in the resonance frequency of the nuclei belonging to the coordination shell with field gradient $\Delta q(r)$. This so called quadrupole effect gives rise to readily observable effects on the NMR signal of the host nuclei.

Three types of NMR measurements can be utilized in investigations of the charge density oscillation around impurities. First there is the measurement of amplitude reduction as a function of the impurity concentration. On statistical considerations the drop in NMR signal amplitude can be given as

$$D = D_o(1 - c)^n \qquad /4/$$

where D and D_o are the signal intensities of the alloy and pure metal and c is the impurity concentration. Parameter n is the wipe-out number given by

$$n = \sum_i^N n_i \, w\,(q_{r_i}) \qquad /5/$$

where n_i is the number of nuclei in the i-th coordination shell and $w(q_{r_i})$ is the contribution to n of a matrix nucleus seen by the field gradient q_{r_i} /Tompa et al., 1969/. At low impurity concentration the so called first order quadrupole effect dominates, and eq/1/ refers only to the satellite contributions of the resonance signal, the central component can be taken as unaffected. We notice here, that the charge density oscillation at a distance of about 20 Å from the impurities, as sensed by the first-order quadrupole effect, which produces wipe-out numbers of 500-2000, can be well accounted for by Friedel's asymptotic expression /1/, though some preasymptotic effects are indicated for Mn and Cr impurities /Grüner, 1972/.

The second type of NMR measurements is line-shape analysis. With the increase of impurity concentration, formerly unobservable distributions caused by the atoms in the coordination shells near to the impurity become observable around the tails of the NMR signals. These distributions change the line shape and lead to a rise in the second moment. It is well known that the relation between the second and fourth moments characterises the

line shape, so that as alloying leads to a Lorentzian-like line shape it must also raise M_4/M_2^2. As both the amplitude reduction and line broadening reflect the average strength of the perturbation, they are nearly independent of the phase φ and are related only to the amplitude α

The third way in which NMR measurement can be used is to observe the satellite structure. The spectra due to nuclei belonging to a single shell have a characteristic structure, which under optimal circumstances may be detected as the satellite lines of continuous wave NMR signals /Alloul et al., 1971; Jánossy and Grüner, 1971/. By comparing the measured with the computed satellite structure, the field gradient at a certain coordination shell around the impurities can be obtained, and this field gradient will reflect both the amplitude α and phase φ of the charge perturbation. The satellites may be measured by the pure quadrupole resonance /PQR/ technique as well /Minier, 1970/.

By measuring the excess second moment, one may gain some information on the tails of the NMR spectrum, and hence on the perturbation at the place of coordination shells near to the impurity. In contrast to the amplitude reduction, which is mainly sensitive to perturbations corresponding to half line width magnitude at the peak-to-peak distance of about 4G, the second moment reflects the perturbation excluding about 20 G, which gives a characteristic distance for this effect of about 10 Å, at which distance the quadrupole shifts given by eq./1/ are about 20 G.

The temperature dependence of the charge density perturbation around impurities has been investigated recently by measuring the temperature dependence of the signal amplitude in Al-3d- transition metal alloys /Grüner and Hargitai, 1971; Grüner, 1972/. While the dependence of α showed a single-peaked distribution, with a maximum between Mn and Cr at $T = 0\ K^{\circ}$, this behaviour became double-peaked at higher temperatures, due to the strong temperature dependence of the charge perturbation around Mn and Cr. This double-peaked behaviour - which reflects the resistivity in noble metal hosts - suggests the development of a double-peaked virtual bound state in aluminium-based alloys. As preasymptotic effects can modify the details of the relation between the signal amplitude and the parameters of the charge perturbation, the measurement of the signal-broadening and its comparison with the amplitude reduction should furnish information about the role of the preasymptotic behaviour of the charge perturbation. This present paper is a report on room-temperature investigations of the line-broadening in Al - 3d-transition metal alloys and its relation to the amplitude reduction measured by one of us /Grüner, 1972/.

EXPERIMENTAL TECHNIQUE

Al-V, Al-Cr, Al-Ti and Al-Mn ingots were prepared from 5-9's Al and 4-9's alloying elements. The measured electrical resistivity showed a homogeneous impurity distribution after annealing at 600 C^{o} and 630 C^{o}, with the possible exception of the Al-Ti /950 ppm/ specimen owing to the presence of some precipitation. The ingots were subsequently cold-rolled into foils of about 15-20 μ thickness and the foils cut into pieces measuring 8x19 mm. The foils were quenched by dropping into water. After the quenching process the foils were assembled into a sample interleaved with insulating paper.

The NMR spectrometer was a field-modulated wide-line spectrometer with a Robinson-type oscillator. Derivatives of the absorption lines were recorded at a fixed frequency /Tompa, 1963/ using a field modulation at 280 Hz. The amplitude of field modulation was 2 Oe. The second and fourth moments of signals were computed in the usual way, taking into account the field modulation correction. The average of second moments was taken of three different positions /0^{o}, 45^{o}, 90^{o}/ with respect to the external magnetic field. This process was carried out to eliminate the slow orientation dependence of signals due to foil-rolling textures /Grüner et al., 1971/. The methods of preparation and NMR measurements of reported experiments are described in this same earlier paper /Grüner et al., 1971/.

RESULTS AND DISCUSSION

The experimental findings for pure aluminium and the alloys will be discussed separately.

1./ Pure aluminium samples

It was established that in pure aluminium, in the absence of impurities, the dislocations and vacancies are dissipated at room temperature. However, identical measurements made by several authors show an intensity reduction and line broadening of NMR signals /increasing second or fourth moment/ that depend on the cold-working and annealing processes /Fernelius, 1966; Grüner and Tompa, 1971; Rowland, 1971/.

The reported data and our own results are collected in Table I. All the measurements listed here were performed a few days after cold-working, annealing and self-recovery, in a state of equilibrium dislocation density. A study of the field dependence of resonance line parameters showed no significant change, so the first-order quadrupole effect was measured.

Since they showed orientation dependence, the spectra were arranged using the theoretical orientation dependence of M_2.

The values listed in the table are much larger than the theoretical Van Vleck second moment /7.6 G^2/. This seems to be due to incompleteness of the self-recovery process in pure Al. Self-annealing can be interfered with by the following effects:

a./ A marked change was observed in the second moments of aluminium samples of different purity /cf. data for specimens N^O1 and N^O2, or N^O8 and N^O11/. A small impurity difference makes a considerable change, therefore the impurities must play an important role in determining the lattice distortion. Part of the line broadening may be explained by charge density oscillation caused by the low impurity content of pure aluminium, the other part might be caused by lattice distortions fixed by impurities /cf. second moment difference between slowly cooled specimens N^O10 and N^O3/. The apparent disturbing effect of impurities on self-annealing depends on the sort of the impurity content as well /Frois, 1962/.

b./ The effect of quenching from different temperature leads to discrepancies in the second moment of specimens of the same purity /cf. specimens N^O11 and N^O12/, and there is a considerable difference in second moments between the quenched and slowly cooled specimens N^O8 and N^O10. The dislocation density after quenching may be high as a result of quenching stress, which depends on the cooling rate and the temperature of quenching /Czizek, 1968/. A part of this dislocation structure can be stabilized by the impurities, as was noted above.

c./ There still remains a considerable difference in the second moments of specimens with the same purity and subjected to the same heat treatment which cannot be explained just on the assumption of the existence of some form effect /cf. specimens N^O1 and N^O5 and specimens N^O1 and N^O7, N^O9/. The form of the specimen may cause two effects. The first is a surface effect, which may be considerable in the case of fine powder specimens; the quadrupole effect associated with surface fields has been investigated by Hughes and Benson /1967/. Secondly, the surfaces are able to contribute to the process of fixing the lattice distortions; this might explain the second moment difference between specimens N^O6 and N^O7. Rowland /1971/ measured the amplitude and second moment of filed pure aluminium powder. From the $/D/Do/\Delta M_2$ ratio we can obtain a special line shape due to lattice distortions /Fig. 2/.

2. Concentration dependence of ΔM_2

Fig. 1 demonstrates a well-observable increase of the second moment resulting from the introduction of various impurities. /Al-Zn was measured by Fernelius /1966/, Al-Ta by Tompa /1969/./ Similarly to the amplitude reduction, the increase of the second moment is due to the first-order perturbation; second-order effects can be neglected. Since ΔM_2 is not a well-defined parameter in alloys, one cannot relate directly the excess second moment to the parameters of the charge perturbation; however, the same signal-to-noise ratio for the specimens allows comparison between the ΔM_2 produced by different impurities. Comparison of the concentration dependence of the signal amplitude and the excess second moment is of particular importance, because it should indicate the variation in behaviour of the charge perturbation around different impurities, as explained in the introduction. Large preasymptotic effects, while giving the same amplitude reduction as in the other cases, influence ΔM_2 in a different way. The plot, in Fig. 2 of the signal amplitude versus the excess second moment for various alloys, including both normal metal and transition impurities, clearly shows that the dependence of D/D_o on ΔM_2 is the same, within experimental accuracy, for all impurities. Thus we conclude that the behaviour of the charge perturbation is similar in all cases, and no drastic preasymptotic effects occur.

In the low-concentration alloys no change was observed in the M_4/M_2^2 ratio and we therefore computed a relation between the amplitude and the second moment by assuming no line shape change. Supposing a Gaussian line-shape, it is easy to find:

$$\Delta M_2 = \frac{M_o}{D/D_o} - M_o \qquad /6/$$

where ΔM_2 is the excess second moment, M_o is the second moment of the pure metal, and D/D_o is the normalized amplitude of the derivative signals. At higher concentrations a marked rise may be observed in the concentration dependence of the excess second moment /see Fig. 1/ and the M_4/M_2^2 ratio /though the error of this value is rather high/. The relation between the second moment and the amplitude measured by us also differs from the computed one. It should be noted that these high concentrations were only relatively high; all of the measured alloys lay within the range of compatibility for the first-order effect. The computed relation between the amplitude and the excess second moment is plotted in Fig. 2. As the experimental points are somewhat above those given by eq./6/, this indicates a line shape change on alloying. The points above the theoretical line must

have a rather Lorentzian line shape, which gives a larger second moment the same amplitude /for a Lorentzian signal ΔM_2 is, in fact, infinite/.

In the light of Fig. 2 it may be deduced that the line broadening exhibits the same main features as the line-amplitude reduction expressed by the first-order wipe-out number n_I.

In the case of Mn and Cr impurities the first-order wipe-out numbers display a double-peaked structure at room temperature /Grüner et al., 1971/ due to the temperature dependence of the charge density oscillation amplitude. While ΔM_2 is not a linear function over the whole temperature range, linearity holds rather well for the lower concentrations /up to a ΔM_2 of about 3 G^2/. Fig. 3 is a plot of values of $\Delta M_2(c)/dc$ versus the impurity atomic number. Though the evaluation of the concentration dependence of $\Delta M_2(c)$ in this way is somewhat arbitrary, the plot shows the same double-peaked distribution, with a minimum at Mn, as with the first-order wipe-out numbers. The validity of the picture given by Fig. 3 is supported by the fact that the ΔM_2 values for Mn lie below these obtained for Fe and Cr impurities in the whole concentration range. This serves as additional confirmatory evidence of the existence of a temperature-dependent charge perturbation around Mn impurities in aluminium.

CONCLUSION

We have measured the second moments of the ^{27}Al NMR line in pure Al after various heat treatments and in several Al-3d alloys. The dependence of ΔM_2 on the purity of the aluminium as well as on the heat treatment points to an effect of lattice distortions. The concentration dependence of the excess second moment is analogue to that of the signal amplitude and indicates a similar charge perturbation around the different impurities. The absence of large preasymptotic effects rules out the possibility of a single Kondo-type narrow resonance in the case of Mn and probably also Cr impurities, and is in clear disagreement with the effective widths derived from the low-temperature macroscopic properties /Caplin and Rizutto, 1968/. This contradiction, which is verified by the measurements reported here, has prompted an attempt to describe in a semi-phenomenological manner the resonance formation in dilute alloys /Grüner and Zawadowski, 1972/. As with the first-order wipe-out numbers, the dependence of $\Delta M_2/dc$ on the impurity atomic numbers shows a double-peaked distribution, which we interpret as arising from the temperature dependence of the charge density oscillation amplitude around the Mn and Cr impurities in Al /Grüner, 1972/.

Since the second moment is not a well-defined parameter in these alloys, such analysis allows only qualitative comparison between the effects of different impurities, and even then only in cases when the resonance lines are measured under similar experimental conditions. It follows that the measurement of the temperature dependence of ΔM_2 cannot be regarded as a meaningful procedure, as the signal-to-noise ratio is a sensitive function of the temperature; instead a detailed line shape analysis is necessary.

Investigations are in progress into the temperature-dependence effects of the charge perturbation by a line shape analysis technique similar to that used in the case of spin perturbation around impurities by NMR method or in evaluating Mössbauer spectra.

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Table I.: NMR Second Moments in Pure Aluminium Samples

Specimen N°	Material source	M_2 [G^2]	Annealing parameters			Reference
			Temperature (C°)	Duration (hours)	Method of cooling	
1.	6-9's powder 4oo mesh	9.7	2oo	2		Al-Zn, Fernelius (1966)
2.	5-9's powder 4oo mesh	1o.3	2oo	2		" " "
3.	5-9's foil 15-2o /u thick ness	8.2	35o	2	slowly cooled	Al-Ta, Tompa (1969)
4.	5-9's powder 325 mesh	17.o	-	-	filed only	Rowland, (1971)
5.	5-9's powder 325 mesh	12.o	25o	15		" "
6.	6-9's powder 325 mesh	19.1	-	-	filed only	" "
7.	6-9's powder 325 mesh	12.5	25o	15		" "
8.	6-9's foil 15-2o /u thick.	8.4	6oo		quenched	Al-Fe, Grüner (1971)
9.	6-9's foil 15-2o /u thick.	8.3	24	-	cold rolled only	" " "
1o.	6-9's foil 15-2o /u thick.	7.8	42o	a week	slowly cooled	" " "
11.	5-9's foil 15-2o /u thick.	8.9	6oo		quenched	Al-Mn, Al-Cr, Al-Ti, Al-V, present work
12.	5-9's foil 15-2o /u thick.	1o.o	63o		quenched	"

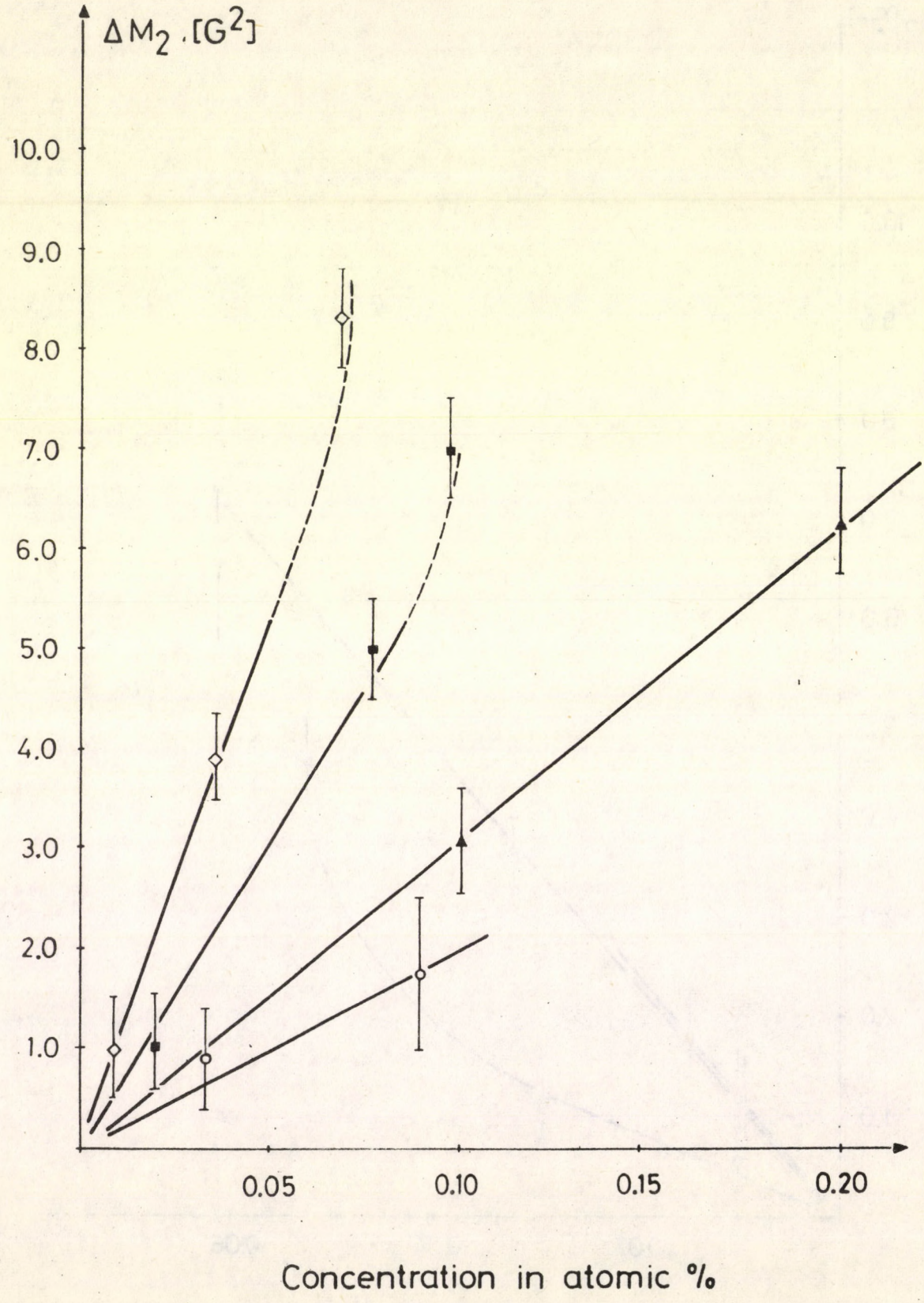


Fig. 1/a Excess second moment ΔM_2 vs. impurity concentration in Al. ΔM_2 is the difference between the second moments of alloy and pure aluminium samples annealed in the same manner
▲ AlCu, o Al-Zn, ■ Al-Ti, ◇ Al-Mn

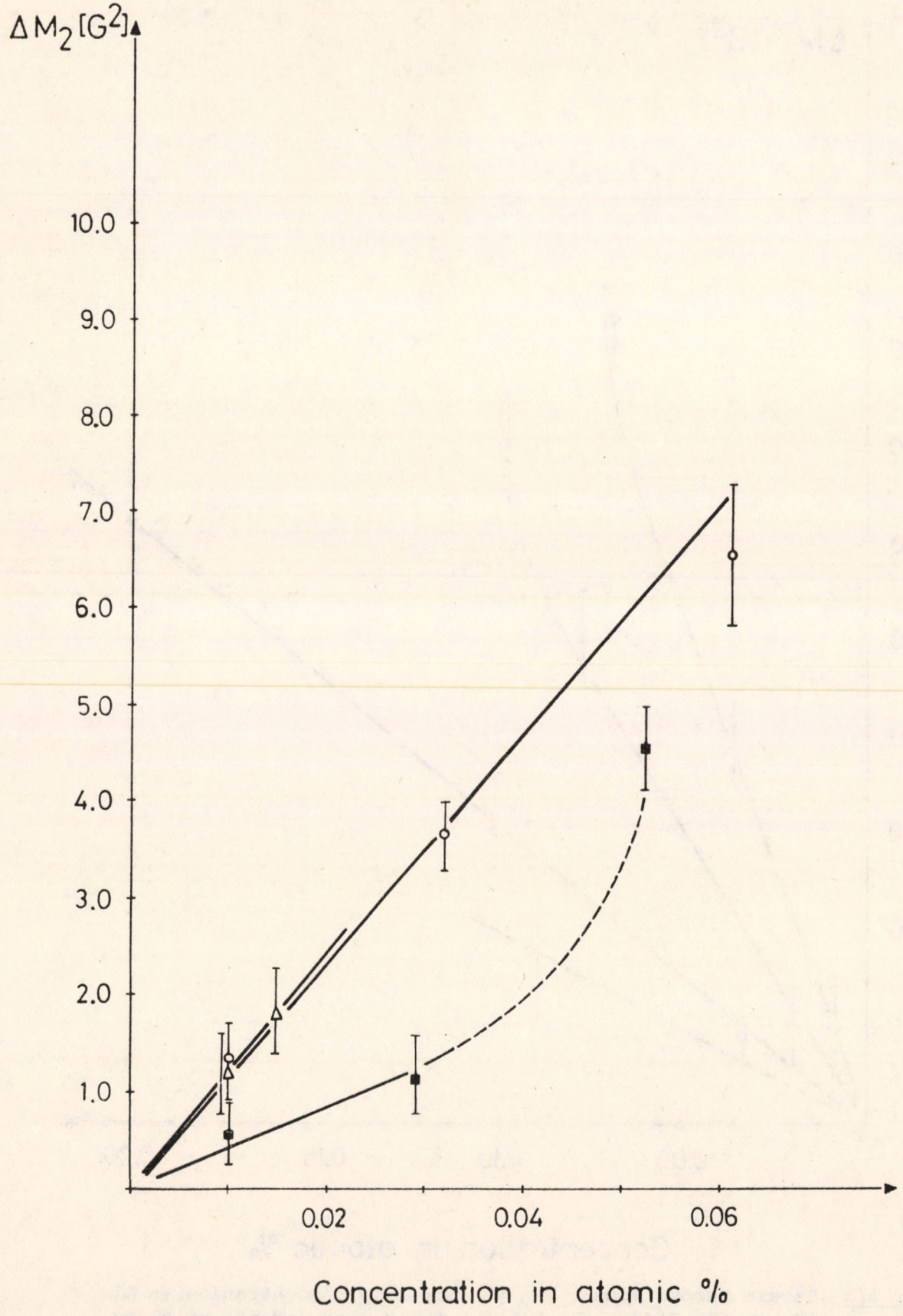


Fig. 1/b Excess second moment vs. impurity concentration in Al.
Δ Al-Fe, o Al-Cr, ■ Al-V

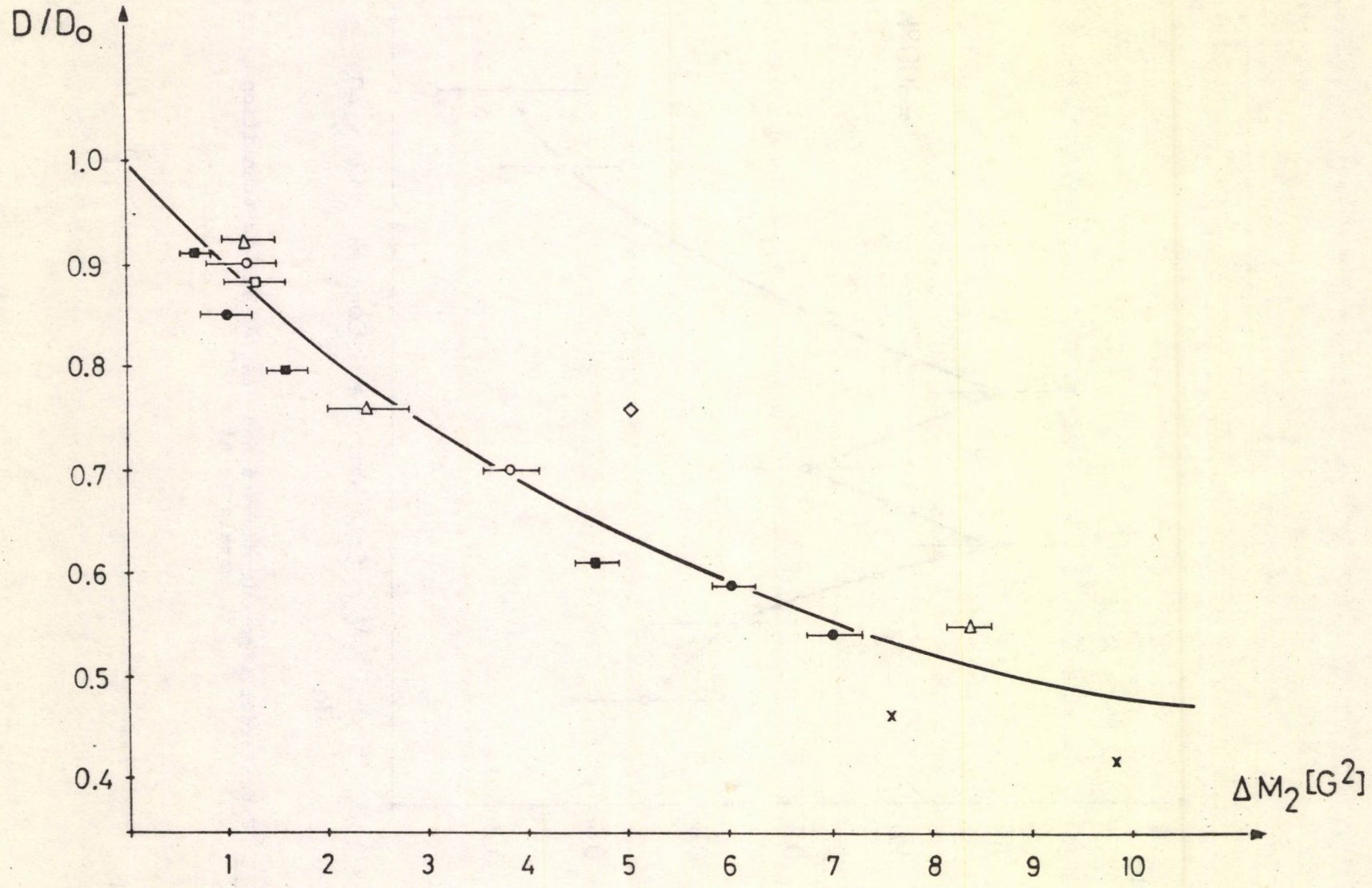


Fig. 2 Peak-to-peak amplitude vs. escess second moment for Al-3d alloys. —— theoretical line, x only cold-rolled Al-Fe alloy /Grüner, 1971/, ◇ only cold-worked pure Al metal /Rowland, 1971/, ○ Al-Cr, △ Al-Mn, ● Al-Ti, ■ Al-V, □ Al-Fe

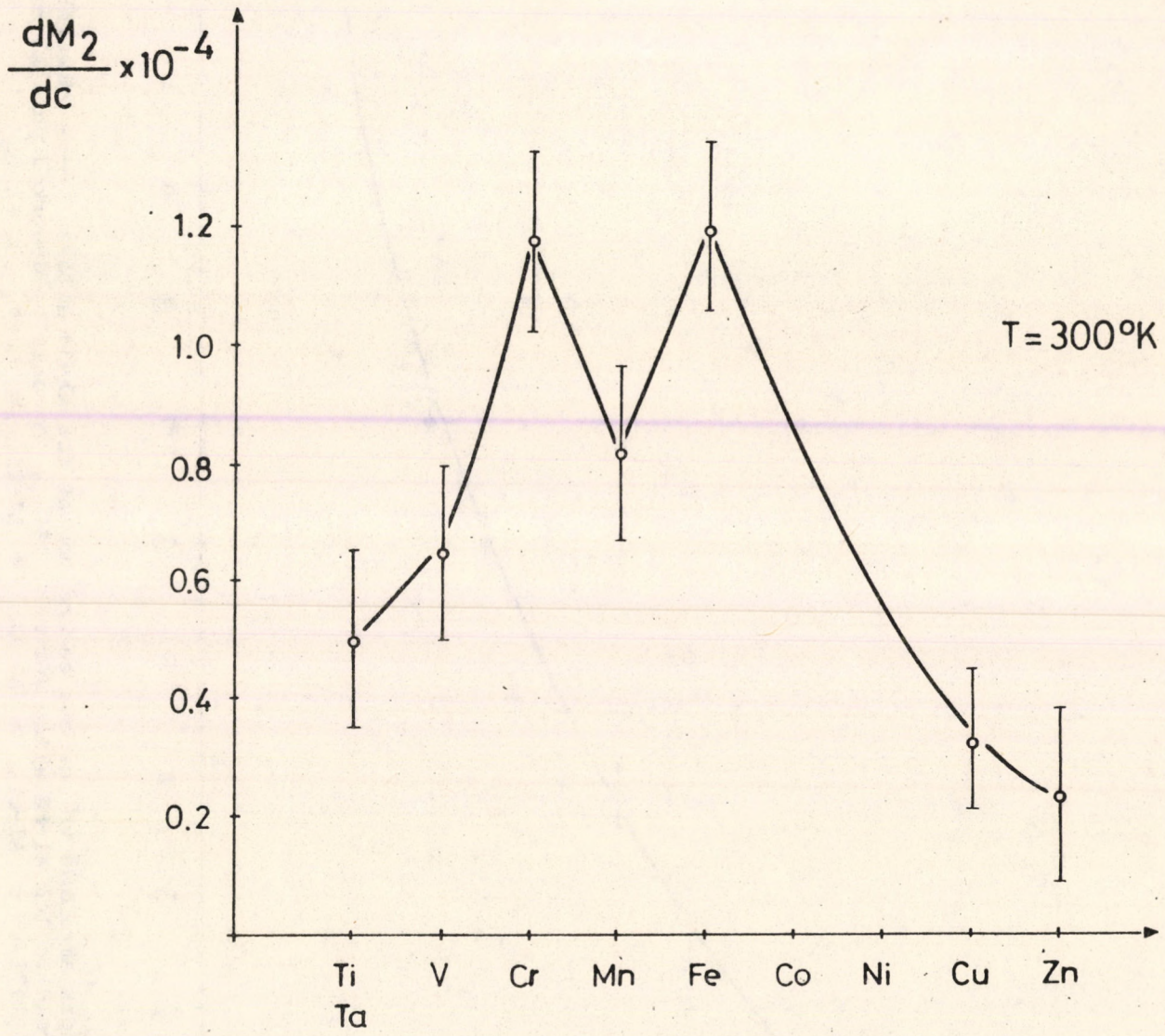
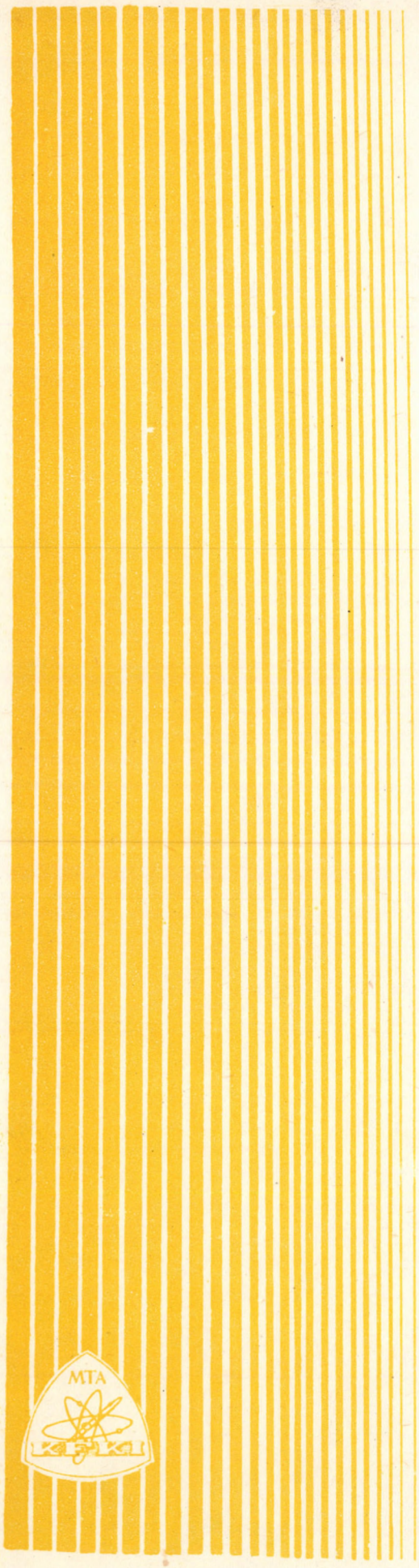


Fig. 3 First-order wipe-out numbers and $\Delta M_2/dc$ for 3d-transition metals in Al



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