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TEMPERATURE DEPENDENCE OF THE CHARGE PERTURBATION AROUND 3d-TRANSITION METAL IMPURITIES IN ALUMINIUM

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ABSTRACT

The temperature dependence of the amplitude α of the charge oscillation around 3d transition metal impurities in aluminium was measured by NMR method. This dependence is strongest in the case of AlMn, where it changes from T^2 to T behaviour at about 300°K. The temperature dependence of the oscillation amplitudes as well as the dependence of α on impurity atomic number imply the change of the character of the virtual bound state at high temperatures.

KIVONAT

A 3d-szennyezések körüli töltéssűrűség α oszcillációs amplitudójának hőmérsékletfüggését mértük aluminiumban, NMR módszerrel. Ez a függés legerősebb AlMn-ben és T^2-ről T-re változik 300 K°-on. Az oszcillációs amplitudók hőmérsékletfüggése, valamint α függése a rendszámtól a virtuálisan kötött állapot megváltozására utal.

РЕЗЮМЕ

В алюминии была измерена температурная зависимость осцилляций электронной плотности вокруг примесей переходных элементов. Эта температурная зависимость самая сильная в AlMn $T < 300^{\circ}K$ его ход меняется по закону T^2 при $> 300^{\circ}K$ идет по линейному закону (пропорционально T). Зависимость амплитуды осцилляций от атомного номера примесей показывают на изменение характера виртуальных связанных d-состояний в AlMn.

The anomalous properties of dilute magnetic alloys have been interpreted mainly in the framework of two limiting cases of the Anderson model [1]. The s-d exchange model, which is derived from the Anderson model when the intraatomic Coulomb energy U is much larger than the width Δ of the virtual bound state /vbs/ [2], has been applied to classical "yes moment" systems like CuFe. The low-temperature nonmagnetic behaviour within this model is due to compensation of the well defined impurity spin by the conduction electrons [3]. The other model regards the impurities as nonmagnetic in the Hartree-Fock approximation /i.e. $Un_d(\varepsilon_F) < 1$ where $n_d\ \varepsilon_F$ is the density of the vbs at the Fermi level/, but near to the condition of the appearance of magnetism and at high temperature the magnetic behaviour is brought about by the localized spin fluctuations /LSF/ [4]. The 3d transition metal impurities in aluminium are regarded as good examples of LSF systems. The impurity Knight shifts and relaxation times [5] show that the susceptibilities are localised on the impurity sites, while the hyperfine field values tend to favour the LSF model over the s-d exchange model [6]. The low-temperature macroscopic properties: the enhancement of the specific heats, susceptibilities [7], superconducting transition temperatures [8] as well as the temperature-dependent impurity resistivities [9] can be explained by the LSF concept.

The subject of the present investigation is the charge perturbation around 3d transition metal impurities in aluminium. This perturbation can be expressed within the

framework of the Anderson model as [10]

$$\Delta\rho(r) = \frac{|V_{kd}|^2}{r^2} \operatorname{Im} \int_{-\infty}^{\infty} f(\omega)\, G_d(\omega) \exp(2ikr)\, d\omega \qquad /1/$$

where V_{kd} is the s-d mixing matrix element, $G_d(\omega)$ the d-electron Green function, and $f(\omega)$ the Fermi function. Expressing the perturbation in terms of one scattering phase shift $\eta_2(\varepsilon_F)$, at $T = 0^oK$ we get the well known Friedel oscillation [10]

$$\Delta\rho(r) = \frac{-\alpha}{2\pi^2} \frac{\cos(2k_F r + \varphi)}{r^3} \qquad /2/$$

at large distances from the impurities, with $\alpha = 5\sin\eta_2(\varepsilon_F)$ and $\varphi = \eta_2(\varepsilon_F)$. At finite temperatures the thermal smearing results in a distance-dependent reduction of the perturbation, and [11]

$$\Delta\rho^T(r) = -\frac{k_F |V_{kd}|^2}{4\pi^3 r^3} \operatorname{Re}\left[G_d(\varepsilon_F) \exp(2ik_F r)\right] \xi/\mathrm{sh}\xi \qquad /3/$$

where $\xi = \frac{2\pi r}{\beta k_F}$. It will be shown later that the distance-dependent reduction of $\Delta\rho^T(r)$ is small and so the tempera-

ture dependence comes mainly from the temperature dependence of the oscillation amplitude. In a previous publication [11] it was reported that the oscillation amplitude α is temperature dependent in the case of Mn and Cr impurities in aluminium. When the vbs is half filled /as appropriate for both Mn and Cr/, Re $G_d(\varepsilon_F) = 0$ and π^{-1} Im $G_d(\varepsilon_F) = n_d(\varepsilon_F)$, and so the oscillation amplitude is proportional to the density of states at the Fermi level. It was suggested that the temperature dependence of α is brought about by the temperature dependence of $n_d(\varepsilon_F)$ due to LSF effects.

This paper reports some further measurements of the charge perturbation around 3d transition metal impurities in aluminium over a broad temperature range and discusses the relation of these experiments to recent resistivity measurements made on AlMn alloys.

The NMR method employed to measure the oscillation amplitude has been described in previous papers [11], [12] and is based on the measurement of the ^{27}Al signal intensity /defined as the peak-to-peak value of the derivative signal/ as a function of the impurity concentration. The charge perturbation gives rise to a field gradient distribution $\Delta q(r) = \frac{8\pi}{3} \mu \Delta\rho(r)$ around the impurities /where μ is the antishielding factor/ and an intensity reduction of the resonance line. The signal intensity D at a concentration c can be expressed as $D = D_o / 1 - c/^n$, where D_o is the signal intensity of the pure metal. The experimentally determined first order quadrupole wipe-out number n depends on the strength of the perturbation. Assuming eq. /2/, n is proportional to α and is nearly insensitive to φ and the former can be evaluated from n by a computer calculation. For the measurements alloys below 1000 ppm impurity concentration were employed. Alloy preparation, heat treatment and analysis have been described elsewhere [14].

Fig. 1 shows the temperature dependence of n in various Al-3d transition metal alloys. /At temperatures below about 250°K small corrections due to eddy current effects [15] were necessary./ This dependence is largest in the case of AlMn and AlCr alloys, while smaller decrease was found for other impurities for which no LSF effects are expected in this temperature range. The temperature dependence of n in AlV and AlTi can be attributed to the effect of the thermal smearing of the host Fermi surface described by $\xi/sh\xi$ in eq. /3/ and to the reduction of the mean free path /mfp/ λ with rising temperature. As the characteristic distance of the first order quadrupole effect corresponding to $n \sim 1500$ is about 20 Å, at 400°K $\xi/sh\xi = 0,97$ and so the thermal smearing gives a reduction in n of about 3%. The finite mfp causes an exponential damping of the charge oscillation in the form [16]

$$\Delta\rho_{\lambda}(r) = \Delta\rho_{\lambda=o}(r)\, e^{-r/\lambda} \qquad /4/$$

The effect of the mfp on the first order wipe-out numbers was computed with eq. /4/ for different α and φ values. The temperature dependence of n coming from the mfp effect can be calculated by evaluating $\lambda(T)$ from the temperature dependence of the resistivity, which in the temperature and concentration ranges of these measurements is dominated by the phonon term. The effect accounts rather well for the measured $n(T)$ in the case of V and Ti impurities. The differences of the n values measured at 200° and 450°K are 140 and 200 in AlTi and AlV alloys, respectively, while the differences computed using eq. /4/ are 130 and 190, which together with the reduction due to the thermal smearing gives 160 and 240. /The larger temperature dependence in the case

of V impurities is due to the larger wipe-out number and hence the larger wipe-out range around these impurities. No temperature dependence has been observed in AlCu and AlSi alloys, due to the small wipe-out numbers 350 and 200, respectively [11]. The temperature dependence of the oscillation amplitude, taking into account the contribution to $n(T)$ coming from the mfp effect and from the thermal smearing of the host Fermi surface, has been evaluated for AlMn. Fig. 2 shows $\alpha(T)$ in AlMn normalised to the value at $T = 0^{\circ}K$, together with the results of recent resistivity measurements [17]. At low temperatures the temperature dependence of α can be described by a T^2 law

$$\alpha(T) = \alpha(T=0)\left[1 - \left(T/\Theta_1^{\alpha}\right)^2\right] \qquad /5/$$

with the characteristic temperature $\Theta_1^{\alpha} = 860^{\circ} \pm 100^{\circ}K$. Above about $300^{\circ}K$ the temperature dependence changes gradually to linear behaviour:

$$\alpha(T) \sim 1 - T/\Theta_2^{\alpha} \qquad /5/$$

which extrapolates to zero at $1400^{\circ}K$. The LSF contribution to the impurity resistivity [17] shows a similar temperature dependence: below $150^{\circ}K$ it is given by $R(T) = R(T=0)\left[1 - \left(T/\Theta_1^{R}\right)^2\right]$, with $\Theta_1^{R} = 530^{\circ}K$, and above $150^{\circ}K$ by $R(T) \sim R(T=0)\left[1 - T/\Theta_2^{R}\right]$ /which extrapolates to zero at about $1600^{\circ}K$/. The temperature dependence of α in AlCr can be fitted with a T^2 law over the whole temperature range with $\Theta_1^{\alpha} = 1400^{\circ} \pm 200^{\circ}K$. Comparing the temperature dependence found in AlV and AlFe and assuming T^2 behaviour, a value of $\Theta_1^{\alpha} \sim 2000^{\circ}K$ can be estimated in the case of Fe impurities.

The characteristic temperatures obtained from the

temperature dependence of the oscillation amplitude can be compared with those evaluated from the anomalous low temperature macroscopic properties. First of all the impurity resistivity is given $R(T) = R(T=0)\left[1 - (T/\Theta_1^R)^2\right]$ with Θ_1^R = = 530°K and 1200°K for Mn and Cr impurities [9].

The enhancement of the susceptibility is reflected by the impurity Knight shift and relaxation time [5]. The d-component of the Knight shift can be expressed by a characteristic temperature Θ_χ as

$$K_d = \mu_B H_{hf}^d \frac{(2b + 1)}{\pi k_B \Theta_\chi} \qquad /7/$$

where H_{nf}^d the hyperfine coupling constant. The values of the d-components of the Knight shifts are -3,6%,-1,7% and -0,7% for Mn, Cr and V impurities, H_{hf}^d =-140kG/μ , giving 450°, 950° and 2200°K for Θ_χ respectively.

The impurity specific heat can be expressed by an empirical law [18]

$$\Delta\gamma/c = A \frac{T}{\Theta_\gamma} \qquad /8/$$

with A = 200 for a broad range of alloy systems such as CuFe, AuV and PdFe. Using the specific heat values obtained by [7] we get Θ_γ = 450°, 620° and 900°K in the case of Mn, Cr and V impurities.

Fig. 3. shows the characteristic temperatures of 3d-transition metal impurities in aluminium, where we have included the characteristic temperatures $\Theta dT_c/dc$ obtained from the superconducting transition temperatures [8]. The logarithmic plot of Θ versus the atomic impurity number shows a V-shaped curve and resembles the situation

; in noble metal hosts [3].

The first order quadrupole wipe out numbers
l at 420°K and extrapolated to T = 0°K are shown in
At zero temperature the dependence of n on the
atomic number shows a single peaked distribution,
aximum between Mn and Cr similarly to the impurity
ity [3], and is in agreement with the Friedel sum rule
degenerate vbs and the phase shifts for the two
ections are equal. At high temperatures however this
ce becomes double peaked, like the impurity resist-
noble metal hosts. Such behaviour is usually re-
s the basic experimental evidence for spin splitt-
he vbs when the impurity is magnetic i.e. $Un_d(\varepsilon_F)>1$.
splitting is represented by phase shifts different
spin up and spin down conduction electrons and the
ximation gives good description for both the resist-
] and charge oscillation amplitude [20] of Cu-3d
on metal alloys. The high temperature behaviour of
tes that similar situation holds in the case of Al-
loys, too, and suggests the onset of the development
ble peaked vbs.

The change of the temperature dependence of the
ng in AlMn from T^2 to T behaviour and the differences
in $\alpha(T)$ and R/T/, should be explained on the basis
SF model, but no properly renormalised theory is
e at present [21]. In this situation we keep only
ical idea of the localised spin fluctuations put
by Caplin and Rizzuto [9] in connection with the tem-
dependence of the impurity resistivity they observ-
Mn and AlCr. Furthermore we consider the relation
the energy and temperature dependence of the den-
states, emphasized first by Hargitai [22]. The nearly
behaviour of the impurities shows up as an enhan-
oth in the static and dynamic properties and can be
ted by an effective width Γ of the density of
The temperature dependence of $nd(\varepsilon_F)$ is determin-
is effective width and [11]

$$n_d^T(\varepsilon_F) = n_d^o(\varepsilon_F)\left[1 - \frac{\pi^2 k_B^2 T^2}{2\Gamma^2}\right] \quad . \qquad /9/$$

With $\Theta_1^\alpha = 860^oK$ we get $\Gamma = 0{,}18eV$, in good agreement with the values derived from the macroscopic parameters [7] [9]. The impurity resistivity being a Fermi surface effect averages out the scattering over an energy range k_BT and reflects both the energy and temperature dependence of $n_d\ \omega$. The conductivity is given by the relaxation time of the conduction electrons $\tau^{-1}(\omega,T) = |V_{kd}|^2\ n_d^T(\omega)$ as

$$\sigma = -\frac{2ne^2}{3m}\int_{-\infty}^{\infty}\frac{df}{d\omega}\,\tau(\omega,T)\,d\omega \quad . \qquad /10/$$

the standard Sommerfeld expansion gives

$$\sigma = -\frac{2ne^2}{3m}\left[\tau(\varepsilon_F,T) + \frac{\pi^2 k_B^2 T^2}{6}\left.\frac{\partial^2\tau(\omega,0)}{\partial\omega^2}\right|_{\omega=\varepsilon_F} + \ldots\right] \qquad /11/$$

Combining eqs./9/ and /11/,

$$R(T) = R(T=0)\left[1 - \frac{5\pi^2}{6}\frac{k_B^2T^2}{\Gamma^2}\right] \qquad /12/$$

and with $\Theta_1^R = 530^oK$ we get $\Gamma = 0{,}14eV$ good in agreement

with the value derived from $\alpha(T)$.

The high temperature behaviour of α and R cannot be described by eqs. /9/ and /11/ as higher order terms to the Sommerfeld expansion have to be taken into account, and only some qualitative remarks can be given. The strong decrease of $n_d(\varepsilon_F)$ should result finally in a double peaked vbs at high temperatures, as the total screening charge

$$\langle n_d \rangle = \int_{-\infty}^{\varepsilon_F} n_d(\omega)\, f(\omega)\, d\omega \qquad /13/$$

remains unchanged. This double peaked vbs is, on the other hand reflected by the high temperature behaviour of n versus the atomic number of the impurities.

The charge of the character of the vbs with temperature indicated by the measurements reported here is one of the most striking aspect of the dilute alloy problem. A phenomenological description of the resonances - based partially on the present experiments - will be published elsewhere [22].

Finally we would like to mention that the high temperature behaviour of n versus the atomic impurity number /Fig.4/ as well as the characteristic temperatures /Fig.3/ suggest a similar situation in the case of noble metal based and aluminium based alloys. Recent careful measurements of the macroscopic parameters well below the characteristic temperatures revealed a same behaviour for a broad range of alloys systems including alloys with rather different temperatures, and the difference shows up only in the temperature range [18]. A similar point of wiew has been stressed recently by Narath on the basis of the impurity Knight shifts and relaxation times of various alloys [23], reinforcing our

conclusion based on the inspection of the high temperature properties of 3d transition metal impurities in aluminium.

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CAPTIONS

Fig. 1. Temperature dependence of the first order wipe-out numbers in Al-3d transition metal alloys.

Fig. 2. Temperature dependence of the oscillation amplitude normalised to the $T = 0^{\circ}K$ value and the LSF contribution to the impurity resistivity /dotted line/ in AlMn.

Fig. 3. Characteristic temperatures of 3d transition metal impurities in aluminium.

Fig. 4. First order wipe-out numbers extrapolated to $T = 0^{\circ}K$ /full line/ and measured at $T = 420^{\circ}K$ /dotted line/. The values for AlCu, AlZn and AlSi alloys are taken from Ref. 11.

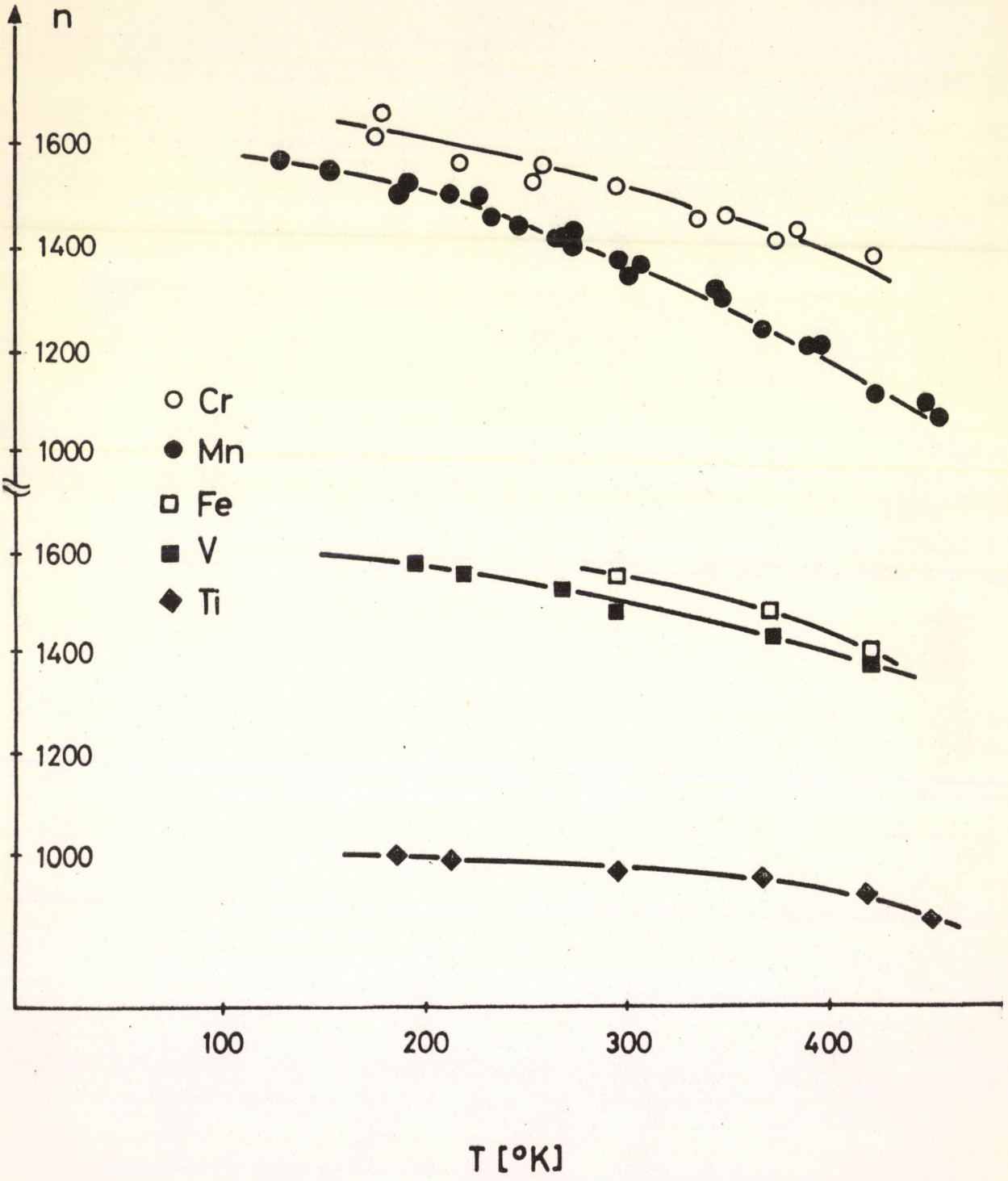
n
1600
1400
1200
1000
1600
1400
1200
1000
Cr
Mn
Fe
V
Ti
100
200
300
400
T [°K]

Fig. 1

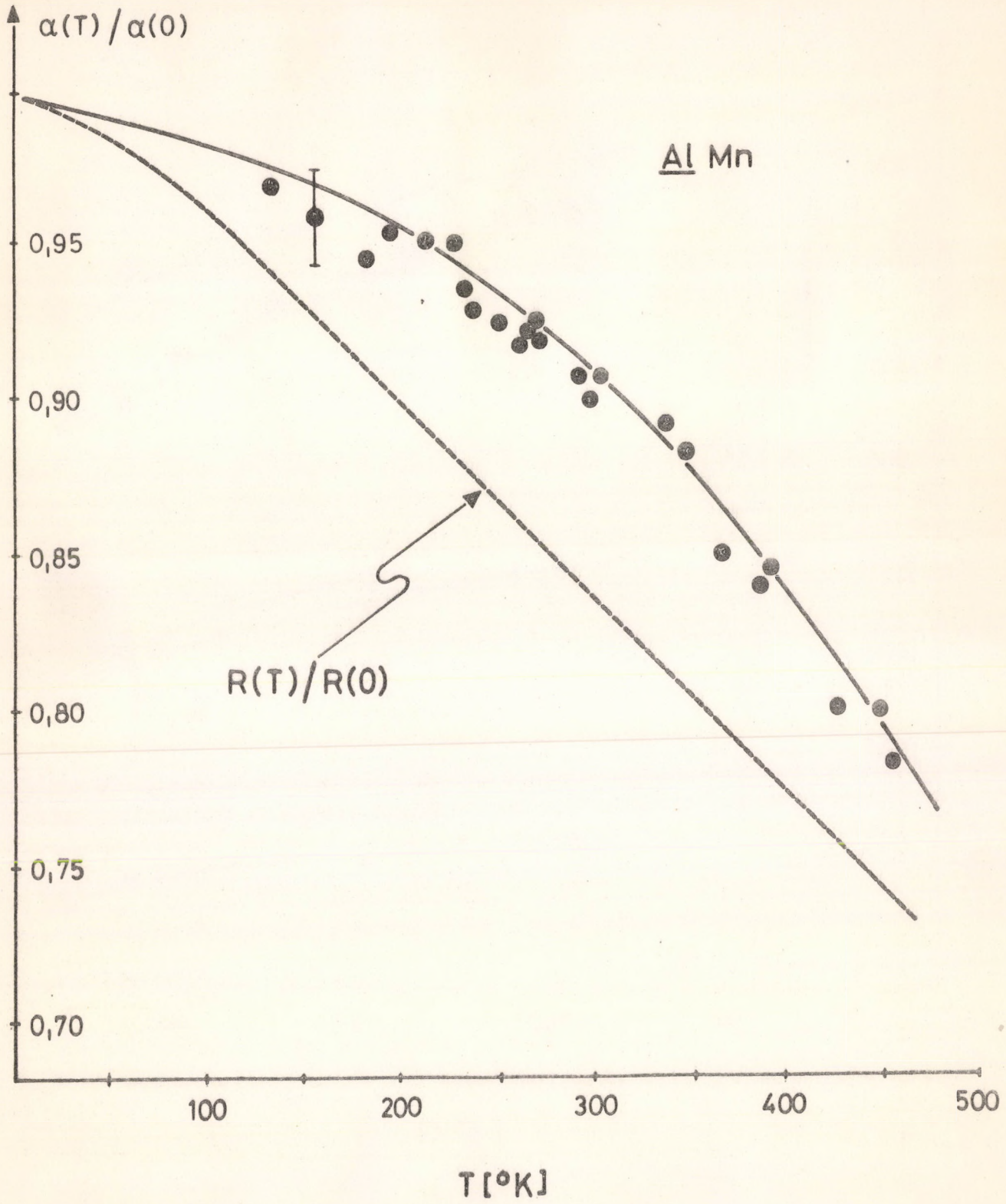

Fig. 2

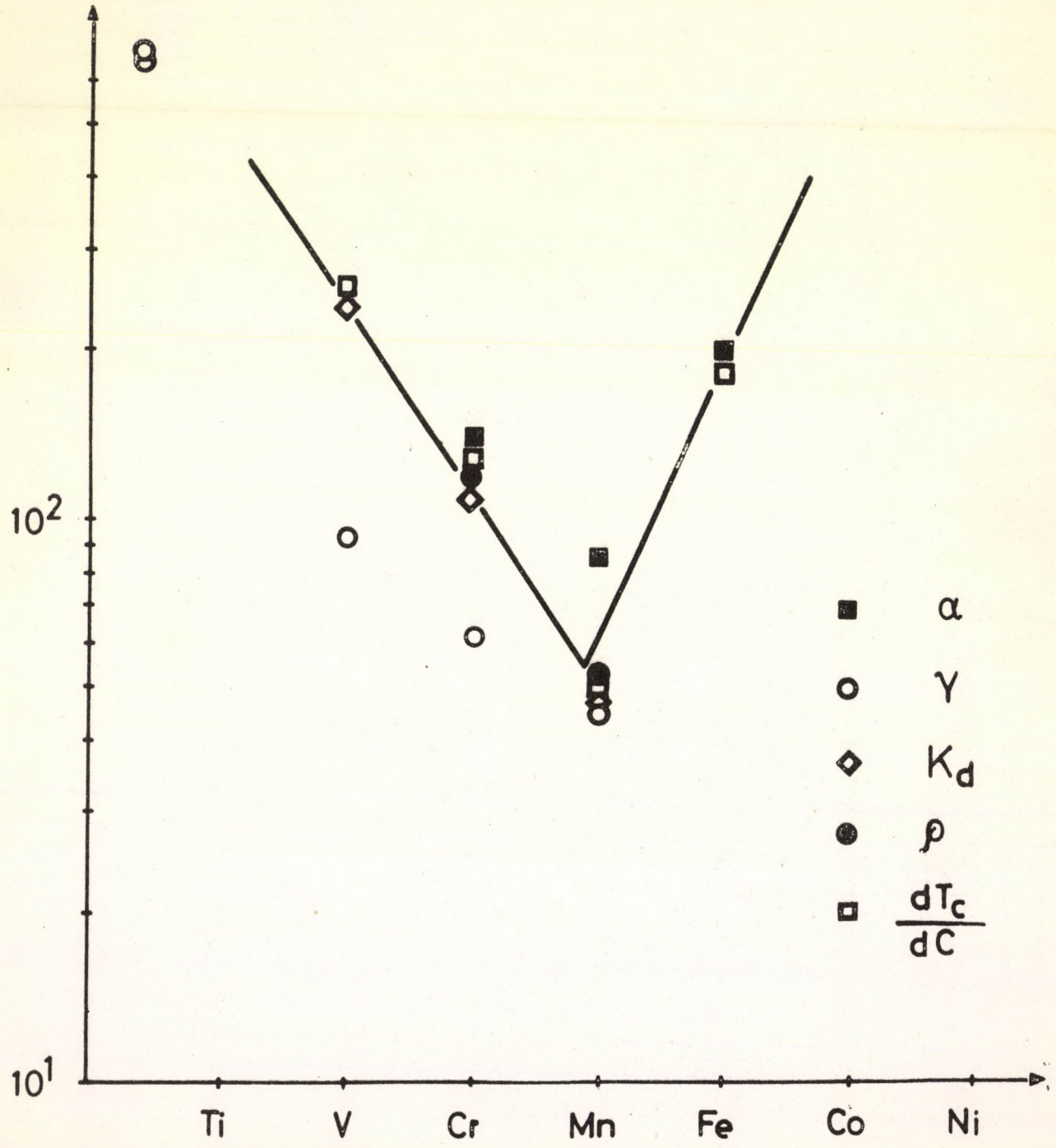

Fig. 3

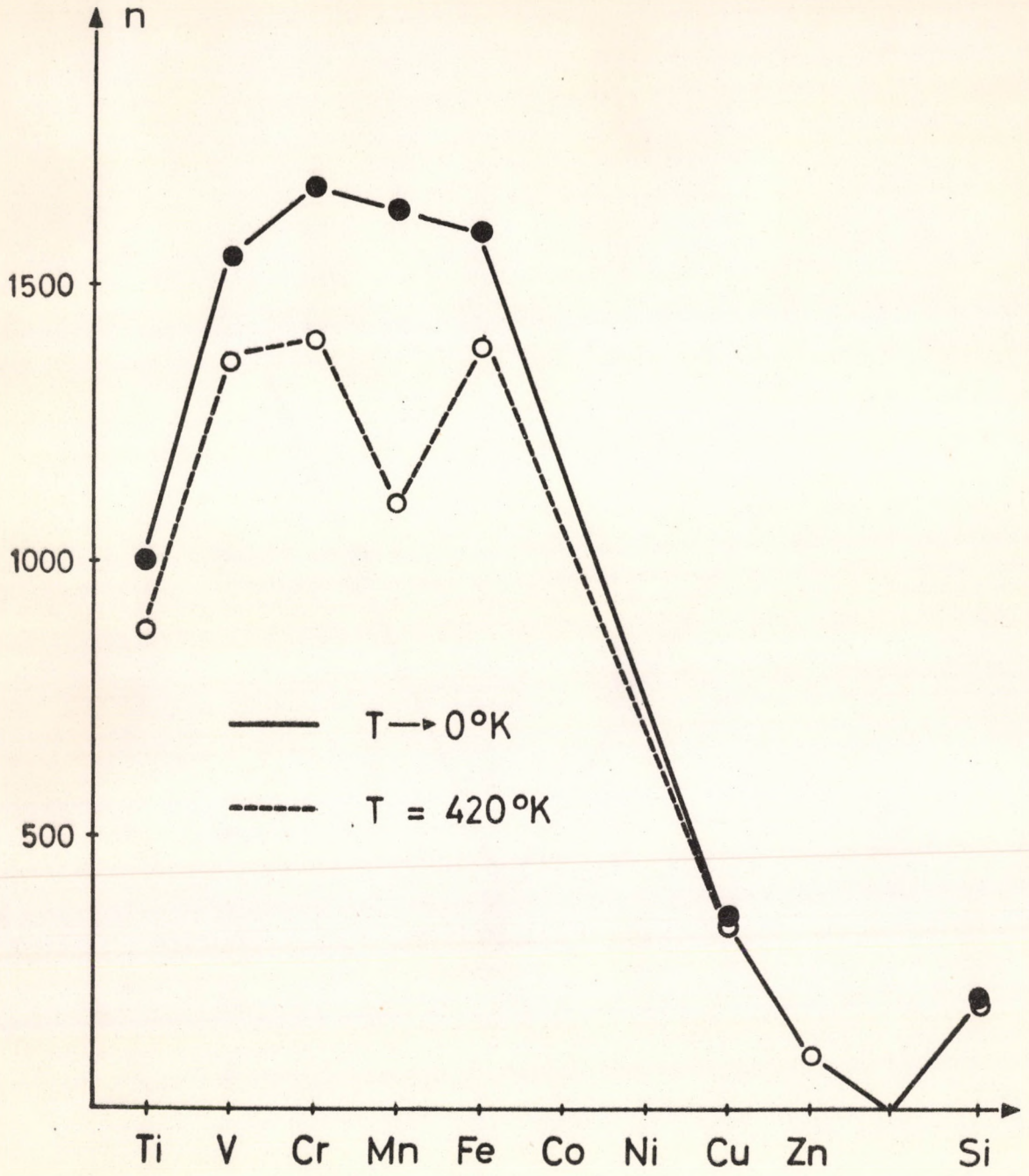

Fig. 4

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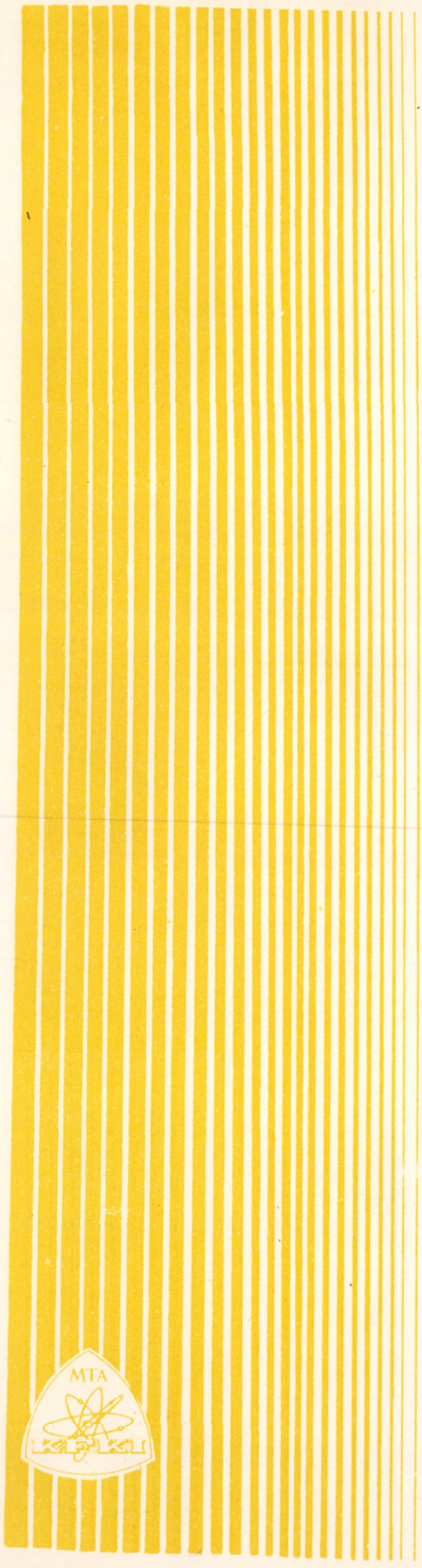

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