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Temperature Dependence of the Charge Oscillation Around Nearly Magnetic Impurities

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In the NMR measurements reported here, it is found that the amplitude of the electron-density oscillation, α, around manganese and chromium impurities in aluminum is temperature dependent. Between 180 and 400°K the temperature dependence can be represented by $\alpha(T)=\alpha(0)[1-(T/\tilde{\Theta})^2]$, with $\tilde{\Theta}\sim 740$°K for manganese and $\tilde{\Theta}\sim 960$°K for chromium impurities. We suggest that this temperature dependence is brought about by the localized spin fluctuations at the impurity sites.

In dilute alloys the impurities are surrounded by an oscillating charge perturbation which can be given, far enough from the impurity, as[1-3]

$$\delta\rho(r)=(\alpha/r^3)\cos(2k_{\mathrm{F}}r+\varphi). \tag{1}$$

In simple theories like the Hartree-Fock approximation of the Anderson model,[4] the amplitude of this oscillation is thought to be independent of temperature whenever there are no magnetic moments on the impurities.[5] In this case the dependence of α on the atomic number Z of impurities can be expressed using the scattering phase shifts of the impurities that are, in turn, simply related to Z through the Friedel sum rule. It is generally accepted that in aluminum the $3d$ transition-metal impurities carry no magnetic moments. One would expect, therefore, that the amplitude of the charge-density oscillation as a function of the atomic number should have a maximum between chromium and manganese. In a recent experiment,[6] however, it was revealed that at room temperature the first-order quadrupole wipeout numbers, which are roughly proportional to α, for the dilute alloys Al:Cr, Al:Mn, and Al:Fe are 1600, 1400, and 1600, respectively. This fact clearly contradicts the Hartree-Fock theory of the Anderson model. Moreover, if the wipeout numbers are supposed to be temperature independent, these room-temperature data contradict even the Friedel sum rule. But, as was shown by Langreth,[7] at $T=0$ the Friedel sum rule is valid in the Anderson model whenever the perturbation expansion in terms of intra-atomic Coulomb interaction, U, can be applied. So the temperature independence of wipeout numbers would invalidate experimentally any perturbation-theoretical approach in the Anderson model even in the nearly magnetic limit. Our purpose was, therefore, to see whether the wipeout numbers for Al:Cr, Al:Mn, and Al:Fe are temperature dependent or not and, if they are, where this temperature dependence comes from.

The redistribution of the electronic charge around impurities yields a field gradient[3]

$$g(\vec{r})=(8\pi/3)\mu\,\delta\rho(\vec{r}), \tag{2}$$

where μ is the enhancement factor (for aluminum $\mu\sim 23$). The distribution of the field gradient gives rise to a reduction of the host NMR signal intensity D, defined as the peak-to-peak amplitude of the derivative signal. At impurity concentration c,

$$D/D_0=(1-c)^n, \tag{3}$$

where n is the signal intensity of the pure host. In aluminum alloys of low impurity concentrations the first-order quadrupole effect dominates, so Eq. (3) refers to the satellite transitions only, and the change of the central component can be neglected. It has been shown[8] that the phase φ in (1) is not essential in the analysis, and the first-order wipeout number n defined in (3) is proportional to the oscillation amplitude α. Therefore, by measuring the signal amplitude of the host nuclei as a function of the impurity concentration, the amplitude of the charge oscillation can be determined.

To obtain the temperature dependence of the oscillation amplitude, we have measured the wipeout numbers at different temperatures in Al-based alloys. The specimens were prepared by melting a master alloy together with pure (99.999+%) aluminum. After cold rolling to about 20 μm the foils were annealed in air for an hour at 600°C and quenched in cold water to obtain homogeneous solid solutions. The concentrations were determined by potentiometric titration and resistivity measurements.

The measurements were performed at an external field of 8 kG with the modulation amplitude $H_m = 2$ G. As a reference the ^{63}Cu resonance in copper foils was used. Compared to this reference signal no temperature dependence was found in pure Al.

In Fig. 1 we present the temperature dependence of the normalized amplitude D/D_0 of the Al^{27} resonance signal for Al:Mn and Al:Cr alloys. For comparison, the results for purely nonmagnetic impurities, copper and silicon, are also given. Since the data are obtained by successive heating and cooling of the samples several times, the reproducibility of the results show that precipitation does not occur in this temperature range.

The data given in Fig. 1 are not corrected for the reduction of the signal amplitude due to the variation of the skin depth at lower temperature. We could detect pronounced asymmetry due to the skin effect only in the case of the sample containing 300 ppm manganese, because of the larger thickness of the foils used. From this and the unpublished data of Jánossy[9] it turns out that at 178°K the reduction of the signal amplitude is about 2%. Above 250°K the skin effect is negligible even in this sample. Though the temperature range is limited by the skin effect at low temperatures and the possibility of the precipitation of impurities at high temperatures, rather strong temperature dependence can be seen for Al:Mn alloys; a little bit weaker dependence can be seen for Al:Cr. From the data given in Fig. 1, taking the logarithmic plot of the signal amplitudes normalized to the satellite transitions, one can determine the first-order wipeout numbers at different temperatures. Figure 2 shows the temperature dependence of n, determined in this way for the different concentrations separately and normalized to the room-temperature values. The rise at lower temperatures for the sample containing 300 ppm manganese is due to the skin effect (with the amplitude reduction discussed earlier taken into account, the corrected wipeout number is about 1550 at 178°K instead of 1660 as given in the figure).

One might at first think that the decrease of the wipeout number with increasing temperature is connected with the decrease of the electronic mean free path.[10] However, the mean free path estimated from the resistivity of these alloys is about 100 Å at 400°K. Within the range of about 100 Å around the impurities, the electron-density oscillation, therefore, is not essentially

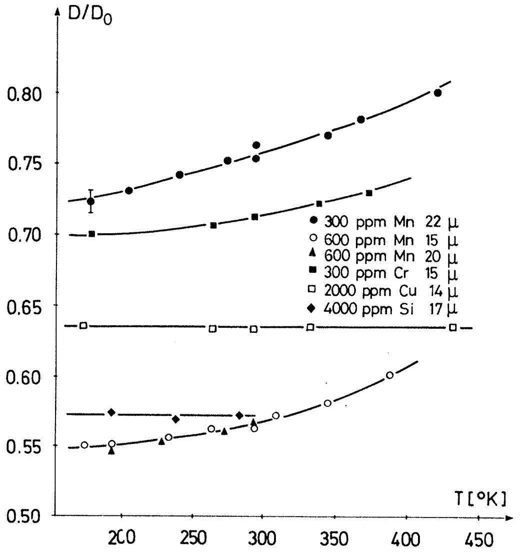

FIG. 1. Temperature dependence of the peak-to-peak intensity of the ^{27}Al absorption derivative in Al:Mn, Al:Cr, Al:Cu, and Al:Si alloys.

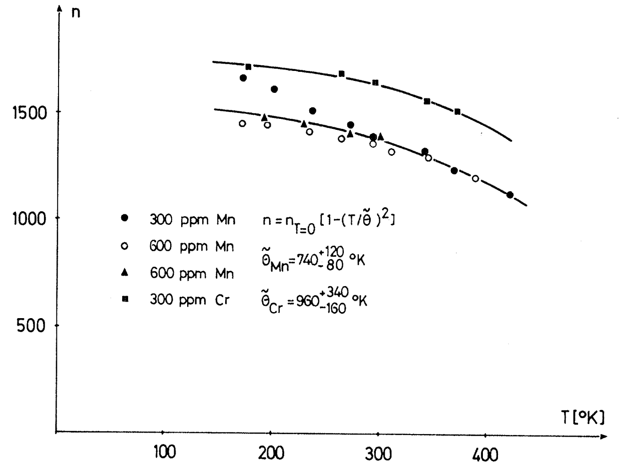

FIG. 2. Temperature dependence of the wipeout number in Al:Mn and Al:Cr alloys. The solid lines represent the temperature dependence theoretically derived, $n(T) = n_{T=0}[1-(T/\tilde{\Theta})^2]$. The parameters $n_{T=0}$ and $\tilde{\Theta}$ consistent with experimental data are chosen.

damped by the mean-free-path effects. So these effects cannot be connected with the decrease of the measured value of n coming from the quadrupole effect on nuclei inside spheres of radius of 20 Å or so around the impurities. Therefore we have to consider the temperature dependence of the wipeout numbers as an inherent property of these impurities.

Let us show that the theory of localized spin fluctuations (LSF)[11] can account for the measured temperature dependence of the amplitude of electron-density oscillation. Using the Anderson Hamiltonian one can prove directly that the electron density around a transition-metal impurity placed at the origin can be given in terms of thermodynamic Green functions[12] as

$$\rho(\vec{r})=\rho_0(\vec{r})+\lim_{\vec{r}\to\vec{r}\,',\ \tau'\to\tau+0}(\beta)^{-1}(2\pi)^{-6}\int d^3k_1d^3k_2\sum_{\sigma}\sum_{\omega_n}V_{\vec{k}_1d}\,G_d{}^{\sigma}(i\omega_n)V_{\vec{k}_2d}G^0(\vec{k}_1;i\omega_n)G^0(\vec{k}_2;i\omega_n)$$
$$\times\exp\{i[\vec{k}_1\cdot\vec{r}-\vec{k}_2\cdot\vec{r}\,'-\omega_n(\tau-\tau')]\}. \qquad (4)$$

Here $\rho_0(\vec{r})$ and $G^0(\vec{k};i\omega_n)=[i(2n+1)\pi/\beta-\epsilon_{\vec{k}}+\mu]^{-1}$ are the electron density and the Green function of the unperturbed host, respectively; $V_{\vec{k}d}$ is the s-d-mixing matrix element, and $G_d{}^{\sigma}(i\omega_n)$ is the Green function of the d electrons virtually bound to the impurity. For the sake of simplicity we assume that $V_{\vec{k}d}=V=\mathrm{const}$ and that the conduction electrons of the host can be described as free electrons. Thus, for the case $\beta k_F{}^2\gg1$ and $k_Fr\gg1$, the approximation first applied by Adawi[13] leads directly to

$$\rho(r)=\rho_0(r)-(\Omega^2/4\pi^2)(V^2/r^3)\,\mathrm{Re}[G_d(\mu+i\delta)\exp(2ik_Fr)](\xi/\sinh\xi)\quad(\xi=2\pi r/\beta k_F). \qquad (5)$$

At low temperatures for impurities with half-filled d levels the LSF theory gives[14]

$$\mathrm{Re}G_d(\mu+i\delta)=0,\quad \mathrm{Im}G_d(\mu+i\delta)=-\Delta^{-1}(1-\pi^2k_B{}^2T^2/2\Gamma^2), \qquad (6)$$

where Δ is the width of the impurity level due the s-d-mixing processes, and Γ is the inverse lifetime of the localized spin fluctuations. So the electron-density oscillation is obtained as

$$\delta\rho(r)=\delta\rho_{T=0}(r)(\xi/\sinh\xi)[1-\pi^2k_B{}^2T^2/2\Gamma^2]=\delta\rho_{T=0}(r)(\xi/\sinh\xi)[1-(T/\tilde{\Theta})^2], \qquad (7)$$

where $\delta\rho_{T=0}(r)$ is the electron-density oscillation caused by the impurity at $T=0$. For the temperature range and distances concerned in the present analysis, the factor $\xi/\sinh\xi\sim1$, so the dominant temperature dependence comes from the variation of the virtual level width due to correlation effects.

It is worth mentioning that for a nearly magnetic impurity with half-filled virtual level, the temperature dependence found in Eq. (7) is determined only by the lifetime of the localized spin fluctuations. For the impurity contribution to the resistivity, $R(T)$, a similar temperature dependence,

$$R(T)=R(T=0)[1-(T/\Theta)^2], \qquad (8)$$

was found experimentally by Caplin and Rizzuto.[15] This temperature dependence comes not only from the temperature dependence of the impurity density of states at the Fermi level but also from the narrowing of the virtual level width due to the correlation effects.[14] Using the LSF theory, one can easily arrive at the following **identity:**

$$\frac{1}{\Theta^2}=\pi^2k_B{}^2\left[\frac{1}{\Gamma^2}+\frac{\pi^2}{75}N_{d,\mathrm{eff}}(\mu)\right]\equiv\frac{2}{\tilde{\Theta}^2}+\frac{\pi^4k_B{}^2}{75}N_{d,\mathrm{eff}}(\mu), \qquad (9)$$

where $N_{d,\mathrm{eff}}(\mu)$ is the effective impurity density of states measured in low-temperature electronic specific-heat measurements. From this last relation, $\tilde{\Theta}$ can be estimated using the measured value[15] of Θ and $N_{d,\mathrm{eff}}$.[16] This estimation gives $\tilde{\Theta}=790$°K for manganese and $\tilde{\Theta}=1330$°K for chromium, in agreement with our data within the experimental accuracy.

Finally, using our experimental data and the relation (7) one can extrapolate the wipeout numbers to $T=0$. The results of the extrapolation are given in Fig. 3 together with the data obtained previously for dilute alloys Al:Cu,[6] Al:Zn,[17] and Al:Ta.[18] The solid line gives the wipeout numbers determined from the resistivity data and normalized to the wipeout number of chromium in aluminum. This figure clearly shows that the dependence of the electronic-density oscillation amplitude on the atomic number is just what the Friedel sum rule predicts. Therefore, for the case of aluminum-based dilute alloys of transition metals the validity of perturbation theory in terms of U is not ruled out experimentally.

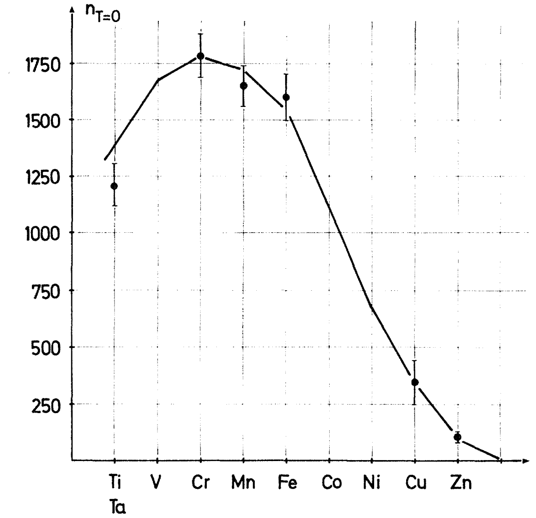

FIG. 3. Wipeout numbers extrapolated to $T = 0$°K for $3d$ transition-metal impurities in aluminum.

The measured temperature dependence of the charge-density oscillation, in our opinion, is brought about by the localized spin fluctuations at the impurity sites. The localized spin fluctuations manifest themselves through the temperature dependence of the impurity density of states at the Fermi level. It is worth mentioning, however, that the whole problem can be formulated also in a little bit different way by replacing $V_{\vec{k}d}G_d{}^\sigma(i\omega_n)V_{\vec{k}'d}$ in Eq. (4) by a temperature-dependent scattering amplitude $t_{\vec{k}\vec{k}'}{}^\sigma(i\omega_n)$. It has already been suggested[19] that in the Kondo model the scattering amplitude behaves like $t_{\vec{k}\vec{k}'}{}^\sigma(T;\mu+i\delta)=t_{\vec{k}\vec{k}'}{}^\sigma(0;\mu+i\delta)[1-\mathrm{const}T^2]$. So the effect reported here, in principle, can also be explained quantitatively in terms of the Kondo model. Unfortunately, in the framework of the Kondo model, one cannot give a numerical estimation of $\tilde{\Theta}$.

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Noncubic Magnetic Anisotropies in Flux-Grown Rare-Earth Iron Garnets

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Torque measurements have been performed on flux-grown magnetic garnets exhibiting strong noncubic anisotropies. The observed orthorhombic anisotropies are interpreted in terms of a growth-induced pair-ordering model.

Flux-grown magnetic garnets containing various combinations of rare earths have been recently reported[1] to exhibit uniaxial magnetic anisotropies of the order of 10^4 erg/cm^3 at room temperature. Noncubic magnetic properties reported previously[2,3] in flux-grown garnets have been attributed to strains induced either during crystalline growth or during sample preparation.