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OSCILLATION OF CONDUCTION ELECTRON DENSITY NEAR THE SOLUTE ATOMS IN DILUTE Cu-Mn ALLOY

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BUDAPEST

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ABSTRACT

The amplitude of the excess charge denstiy around solute Mn atoms in dilute copper based alloy is evaluated from the experimental wipeout number $n_s = 1000 \pm 20$ %, characterizing the first order quadrupole effect of the ^{63}Cu NMR spectrum. Assuming an enhancement factor $\alpha = 25$, the amplitude is about 2,1 times that measured for CuZn and agrees within a factor of 1,5 with the value predicted in terms of the Blandin-Caroli resonance scattering theory.

The experimental aim was the observation of the parameters characterizing the excess conduction electron density near the solute Mn atoms in copper based alloy by measuring the first order quadrupole effect appearing in the ^{63}Cu NMR spectrum [1]. The charge denstiy oscillation which is expercted to be zero in terms of the s-d exchange model in first approximation /see e.g. [2]/, is nonzero in terms of the theory of virtual bound states /see e.g. [3]/. The latter prediction was experimentally confirmed by the second order quadrupole effect measurements of Lumpkin [4]. On the other hand, one way for the experimental check of the most recent approach of the Kondo-type systems /see e.g. [5]/ could be the direct observation of the oscillation of the conduction electron charge and spin densities around the impurities in the temperature range in question.

In the case of very dilute alloys the only useful NMR technique for the observation of the charge density oscillation seems to be the measurement of the concentration dependence of the signal amplitude. The study of alloys exhibiting first order effect was chosen for two reasons, namely

a/ very dilute alloys can be investigated,

b/ the effect of charge density oscillation is not arbitrarily separated, like in the region of second order interactions, from that of the spin density oscillation caused by the localized moment.

In this short communication we present our preliminary result on Cu-Mn dilute alloys. The measurements were performed on $\sim 20\ \mu$ thick foils produced by cold rolling. The master alloy was prepared from 99,998 at.% copper and 99,9 at.% manganese by vacuum smelting [6]. To remove dislocation effects the specimens were annealed for 1 hour at 400 °C. The duration and temperature of the annealing was chosen to be such in order to avoid the internal oxidation observed by Howling [7]. The Mn concentration of the dilute specimens, determined by activation analysis was found to be 230 and 690 at.ppm Mn /$\pm$10 %/.

In order to separate the quadrupole effect from that originating from magnetic interactions, the measurements were performed at temperatures from 150° to 300°K, thus well above the Kondo temperature, and the magnetic field /4...10 kOe/ dependence of the signal amplitude was measured at room temperature. The spectrometer described in [8] was used. The experimental points are averages taken over about 50 spectra measured in different directions. Simultaneously measured ^{27}Al NMR signals from Al foils were used as reference. The measured amplitudes are normalized to that of pure copper.

Within the experimental accuracy the peak-to-peak amplitudes vary linearly with the external magnetic field and the inverse temperature. The concentration dependence shown in Fig. 1 was plotted for the amplitudes extrapolated to zero field or infinite temperature. The concentration dependence of the extrapolated values was used for the evaluation of the wipeout number $n_s = 1000 \pm 20$ %, the characteristic parameter of the first order quadrupole effect which is independent of field and temperature.

The measured H/T dependence of the amplitudes resulting from the magnetic moment locaoized on the Mn atom permits to evaluate the oscillation of spin denstiy, as will be shown in a forthcoming paper.

Assuming the sacttering to be predominantly d-resonance scattering, the excess density of the conduction electrons with spin σ near the impurity is given by the expression [3] as

$$\Delta\rho^{\sigma}(r) = -\frac{5}{4\pi^2} \sin \delta_2^{\sigma}\, r^{-3} \cos\left(2k_F r + \delta_2^{\sigma}\right)$$

where r is the distance, k_F the Fermi wave number, while the phase shifts δ_2^{σ} of the scattered partial waves $\ell = 2$, taken at the Fermi energy, are related to the number of localized d-electrons through the expression $N = \frac{5}{\pi}\left(\delta_2^{\uparrow} + \delta_2^{\downarrow}\right)$ and to the component z of the magnetic moment localized on the impurity atoms through the formula $M_z = -5\frac{\mu_B}{\pi}\left(\delta_2^{\uparrow} - \delta_2^{\downarrow}\right)$ / μ_B is the Bohr magneton/.

The difference in the number of spin-up and spin-down electrons gives the spin density-, while their sum the charge density oscillation. Thus, the component z of the electric field gradient can be expressed as

$$q = \frac{8\pi}{3} \alpha \left[\Delta\rho^{\uparrow}(r) + \Delta\rho^{\downarrow}(r) \right]$$

where α is the enhancement factor, [9].

Usign the phase shifts

$$\delta_2^{\uparrow} = \pi \; ; \quad \delta_2^{\downarrow} = \frac{\pi}{5} \cdot 0,7 = 0,44$$

given by Daniel [10] in connection with the calculation of the residual resistivity in 3d - Cu alloys, the excess spin-up electron density is zero and the excess charge density is contributed by spin-down electrons as

$$\Delta\rho(r) = \Delta\rho^{\downarrow}(r) = -5.10^{-2} \; r^{-3} \cos\left(2k_F r + 0,44\right)$$

This result was compared with the prediction from the second model described in [11].

The physically much more realistic b/ model, in which the first order wipeout number is hardly dependent on the oscillation phase, relates the oscillation amplitude directly to the wipeout number if the value of α is known. The amplitude of the excess charge density evaluated with the assumption of $\alpha = 25$ from the wipeout number gives $3,4 \cdot 10^{-2}$ in fair agreement with the calculated $5 \cdot 10^{-2}$. /In the all-or-nothing model the parameter $q_{crit} = 1,8 \cdot 10^{21}$ cm^{-3} which is in agreement with the value for CuZn./

Additional contributions from the s-, p-scattering and the scattering from displaced matrix atoms, will be estimated in a forthcoming paper.

The quadrupole effect of the NMR of the matrix nuclei in dilute alloys of copper with 3-d transition metals can be easily estimated from resonance scattering theory, using e.g. the phase shifts determined by [10] or by making use of the assumptions about the electronic structure of 3-d transition metals embedded in copper [12].

Above the Kondo temperature the dependence of the excess charge density near the solute atoms on the atomic number of the latter yields

a V-shaped curve with manganese at the minimum. Assuming full decoupling of virtual levels, it is found that the excess charge density in the case of Mn-Fe-Co is contributed by electrons with spin-down and in the case of Cr-V by electrons with spin-up.

The quadrupole effects in these alloys are excepted to show similar behaviours as the impurity contribution to resistivity below the Kondo temperature too [13].

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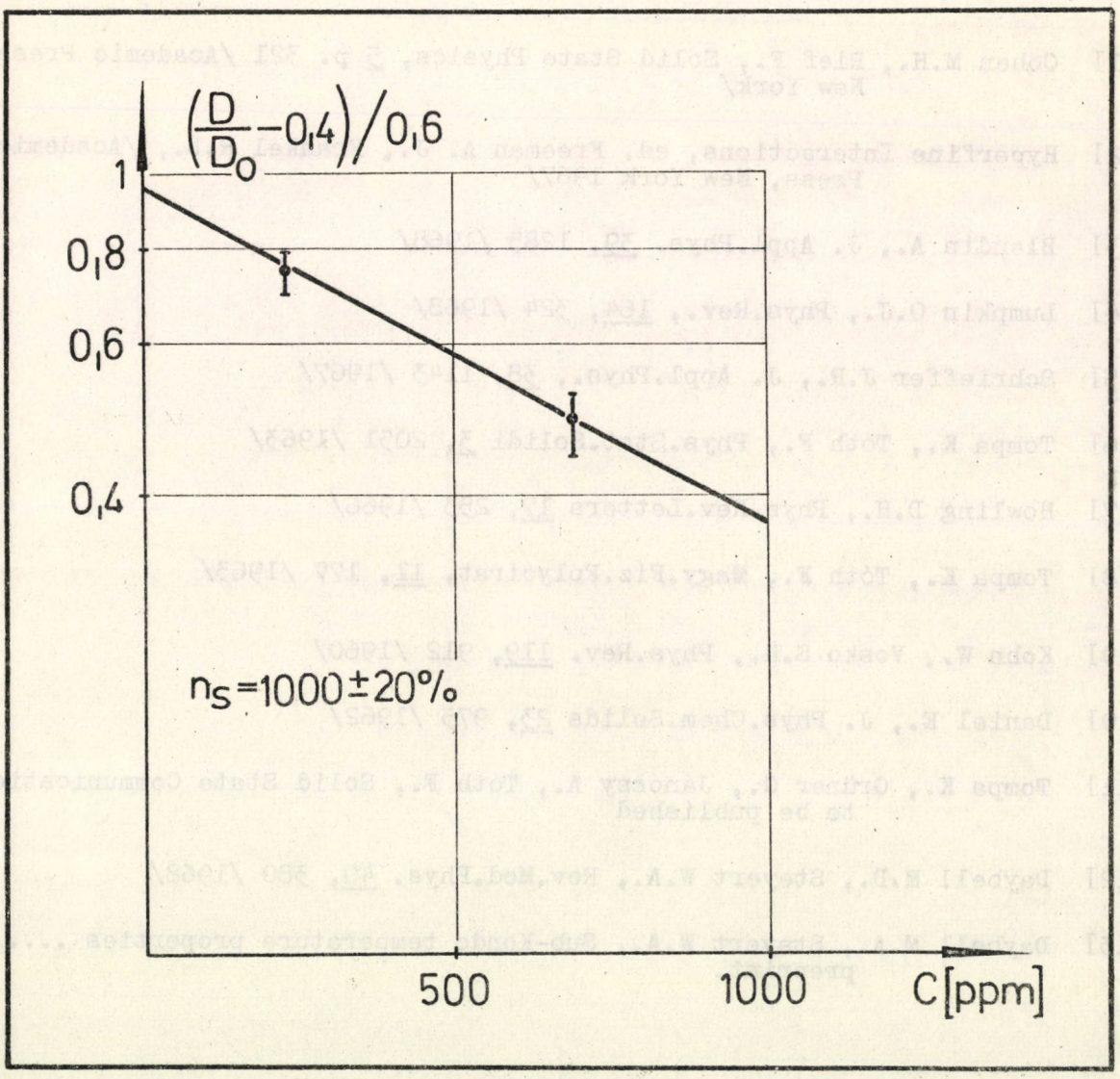

Fig. 1

First order quadrupole effect in copper based Cu-Mn dilute alloys

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