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^{63}Cu NMR in ELASTICALLY DEFORMED COPPER FOILS

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Summary

The ^{63}Cu NMR spectrum parameters are, within the experimental accuracy, the same for the undeformed as for the in the $\langle 100 \rangle_{av}$ direction up to the elastic limit stretched samples. The data were taken on a copper foil of cubic texture, characterized by an average deviation of about 6,5 degrees. Our results with the application of the Sholl theory of the quadrupole effect in metals give an upper limit for the antishielding factor $(1-\gamma_\infty)$.

Introduction

The investigation of the quadrupole effects in the NMR spectrum can yield valuable information about the electron structure of solids, in our case of metals and alloys. In cubic crystals, free of deformation and impurity effects the electric field gradient at the nuclei is exactly zero so quadrupole effects are informative only, if the cubic symmetry is destroyed artificially, e.g. by the introduction of impurities, lattice defects or by the application of elastic strain. The electric field gradient so appearing is characteristic to the electron structure.

Such experiments were already done on copper making use of each of the three previous possibilities, all of them being evaluated however by the point-charge model only, i.e. by the comparison with the electric field gradient produced by bare copper ions of charge +e, situated on lattice points. /For the case of impurities our subsequent discussion shall deal only with the "size-effect"./ The parameter λ , the quotient of the field gradient measured and calculated from the point-charge model was not interpreted theoretically, attention having been called to the fact only, that it is not identical with the Steinheimer antishielding factor, $(1-\gamma_\infty)$, the difference being due to the conduction electrons.

The experiments gave for λ a very broad interval indeed, with 60 the upper and 0,4 the lower bound.

a/ Bloembergen [1] obtained on dilute alloys a value $\lambda = 60$, considering the size effect only. Sagalyn and coworkers [2] obtained either $\lambda = -15$, or $|\lambda| = 6,7$, dependent on the superposition of the "size" and "charge" effects.

b/ On plastically deformed foils Faulkner [3] got a $\lambda \geq 0,4$, the reevaluation of these date by Ogurtani el al [4] led to a $\lambda = 0,4$, while Averbuch et al [5] obtained $\lambda = 1,2$ on filed unannealed powder samples.

c/ Faulkner [6] estimated an upper bound, $\lambda < 7$ from the study of elastically deformed foils of isotropic crystallite orientation.

The point charge model used in all these comparisons was also somewhat rudimentary, the summations being performed for the first neighbours only.

Experiment

The quadrupole effect in copper could be studied most directly in uniformally strained single crystals. Instead of this, we investigated copper foils of cubic texture, as we had done before [7]. The stretching direction coincides approximately with the $\langle 100 \rangle_{av}$ type directions of the crystallites, this direction being denoted by the symbol $\langle 100 \rangle_{av}$. The deviation of the individual crystallite <100> directions from $\langle 100 \rangle_{av}$ is always below $6,5^{o}$ [8]. This deviation was not taken into account during the evaluation of the data.

Measurements were made on room temperature at a frequency of 6,5 MHz by a wide line NMR spectrometer [9], where in order to increase the signal to noise ratio an analog integrator circuit was used after the phase sensitive detector [10]. The sensitivity of the arrangement can be assessed from Fig. 1., which shows the ^{63}Cu NMR signal, detected on a foil sample of about 40 milligrams effective mass.

The sample and its holder are to be seen in Fig. 2. In order to achieve an homogeneous strain, only the ends of the foil are fixed, the roller at the turning points making an easy displacement of the foil possible. The cross section of the foil was 20 microns by 8 millimeters, the total cross section its fourfold, the load being 3,1 kp. The strain calculated with a Young modulus $E = 12,500$ kp/mm^2, is $3,8 \cdot 10^{-4}$, corresponding for a soft foil to a stretching up to the elastic limit [11].

The constant magnetic field was perpendicular to the stretching direction.

It was found that the NMR spectrum of the undeformed and of up to the elastic limit in $\langle 100 \rangle_{av}$ direction stretched samples were, in regard both of amplitude and second moment, the same.

Theory

Assuming an homogeneous deformation in the effective volume of the sample, i.e. and identical field gradient at the nuclei contributing to the resonance, a first order quadrupole effect is to be expected. /The possibility proposed by Faulkner, that the satellites do not contribute even in a well annealed sample to the integrated intensity, may be excluded by our study on dilute Cu-Pt alloys [12]. /The frequency shift of the satellities for an axially symmetrical electrical field gradient in the x direction is given by [13]:

$$\Delta\nu = (2m - 1)(3\cos^2\theta - 1)\,\frac{3e\,Q}{8J(2I-1)h}\,\phi_{xx} \qquad /1/$$

where e is the elementary charge, h Planck's constant, I the nuclear spin, Q the nuclear electric quadrupole moment, m the magnetic quantum number, ϕ_{xx} is the field gradient in the x direction, θ the angle between the constant magnetic field and the x axis.

The frequency shift for a spin $I = 3/2$, and $\theta = 90^\circ$ reads

$$\Delta\nu = \pm\,\frac{eQ}{4h}\,\phi_{xx} \qquad /2/$$

The field gradient is now calculated in the point-charge approximation a/ with Sholl's model b/ and by applying the phenomenological theory c/.

a/ The point-charge model

The formula is simply:

$$\phi_{xx} = \lambda'\,\phi_{xx}' = \lambda' \sum_i \frac{e_i\,(3\cos^2\theta_i' - 1)}{r_i^{\,3}} \qquad /3/$$

where e_i is the charge on the i-th ion, +e in our case, r_i' the position vector, θ_i' the angle between r_i' and x, λ being an empirical parameter. Retaining the terms linear in the deformations:

$$\phi_{xx}' = e\varepsilon(1+\nu)\,3 \sum_i \frac{1}{r_i'^{\,3}} \sin^2\theta_i\,(5\cos^2\theta_i - 1) \qquad /4/$$

where the unprimed quantities, r_i and θ_i, pertain to the undeformed lattice, ε denoting the relative elongation in the $<100>_{av}$ direction and ν the Poisson-number (ν=0,35). Performing the summations for the first n coordination shells by a digital computer we get:

$$\phi_{xx} = e\left(\frac{2}{a}\right)^3 K^{(n)} \varepsilon(1+\nu) \qquad /5/$$

where $a = 3{,}61 \cdot 10^{-8}$ cm is the lattice constant, the numerical values being $K^{(1)} = 2{,}12$, $K^{(2)} = 0{,}62$, ... $K^{(100)} = 1{,}28$.
Our result for the first coordination shell is in agreement with the corresponding results of references [6] and [2].

b/ The field gradient calculated by the Sholl theory

The theory states that the field gradient at the nuclei is the sum of the appropriate derivatives of the oscillating screened potentials due to all the other ions, and can be calculated without an explicit knowledge of the eigenfunctions themselves [14]. The axial electrical field gradient is given by

$$\phi_{xx} = (1 - \gamma_\infty) \sum_i v_2(r_i')(\cos^2\theta_i' - 1/3)$$

$$v_2(r_i') = \frac{A(2k_F)^2}{(2k_F\, r_i')^5}\{7\,(2k_F\, r_i')^2 \sin(2k_F\, r_i') + \qquad /6/$$

$$+ [15 - (2k_F\, r_i')^2] \cos(2k_F\, r_i')\}$$

where r_i', θ_i' are the same as before, k_F is the Fermi wave - number, $(1-\gamma_\infty)$ the antishielding parameter, A the amplitude of the oscillating potential.

For an unscreened Coulomb potential the value of A is given by

$$A = \frac{2Z\, m\, e^3}{\pi\, \hbar^2\, \varepsilon^2(2k_F)} \qquad /7/$$

where m is the free electron mass, $\hbar = \frac{h}{2\pi}$, $\varepsilon(2k_F)$ denoting the value of the dielectric function at a wave number $q = 2k_F$

$$\varepsilon(2k_F) = 1 + \frac{m\, e^2}{2\pi\, k_F\, \hbar^2} \qquad /8/$$

The oscillation in the potential is due to the singularity of the dielectric function at $q = 2k_F$, the detailed form of the unscreened potential influencing only the magnitude of A.

Applying now this theory to copper monocrystals stretched in the <100> direction and retaining only the linear terms, we get

$$\phi_{xx} = (1-\gamma_\infty)\,\varepsilon(1+\nu) \sum_i v_2(r_i) \sin^2\theta_i \,(5\cos^2\theta_i - 1) \qquad /9/$$

r_i and θ_i pertaining again to the undeformed lattice.

The value of the antishielding parameter, $(1-\gamma_\infty)$ is unknown for metallic copper, but it can be reasonably supposed that it is larger, than the value 16, calculated by Steinheimer [15] for the free cuprous ion.

Performing the indicated summation in (9), and denoting the sum for the first n coordination shells divided through $A(2k_F)^2$ by S^n, the following results were obtained

$$S^1 = 0{,}02244 \qquad S^{100} = -0{,}00468.$$

$$S^{1000} = -0{,}00348$$

c/ Field gradient-strain tensor approach

The required field gradient in dependence on the strain can be easily determined with the help of the phenomenological theory of Shulman at al [16], and Sagalyn at al [2]. The field gradient components contributing to quadrupolar interaction are of the following form:

$$\phi_{ij} = (F_{11} - F_{12})\,\delta_{ij}\,[\varepsilon_{ij} - \tfrac{1}{3}\sum_1 \varepsilon_{11}] + 2\,(1 - \delta_{ij})\,F_{44}\,\varepsilon_{ij} \quad , \qquad /10/$$

where F_{ij} are the components of the field gradient-strain tensor, ε_{ij} those of the strain tensor, δ_{ij} the Kronecker-function.

With assuming isotropy, i.e. $F_{44} = \frac{1}{2}(F_{11} - F_{12})$ the number of independent F_{ij} components can be reduced further. In our case, however it is superfluous to take into account the assumed isotropy, since the second term on the right side of /10/cancels in ϕ_{xx} . With the previously used $\varepsilon_{xx}=\varepsilon$, $\varepsilon_{yy}=\varepsilon_{zz} = -\nu\varepsilon$ notations we finally get:

$$\phi_{xx} = \tfrac{2}{3}(F_{11} - F_{12})\,\varepsilon\,(1 + \nu) \qquad /11/$$

/11/ shows immediately, that the dependence on the deformation must contain the factor $\varepsilon(1+\nu)$, as in fact, already obtained in our Eqs. /4/ and /9/. Comparing Eq. /11/ with the results obtained by the application of the point-charge model, the quality $(F_{11}-F_{12})$ can be expressed by atomic constants and the empirical parameter λ' .

If however one compares Eq. /11/ with Eq. /9/ the quantity $F_{11}-F_{12}$ can be determined theoretically, without any arbitrary constants. From the above it follows that the empirical parameter λ' is in reality superfluous and can be dispensed with. In our treatment emphasis is laid on the anti-shielding parameter $(1 - \gamma_\infty)$, which can be theoretically determined in principle.

Evaluation of the data

For a substantial satellite shift, $\Delta\nu$ can be immediately obtained, yielding the experimental values either for λ' or for $(1 - \gamma_\infty)$.

For shifts smaller than the resonance line width $\Delta\nu$,i.e. λ' and $(1 - \gamma_\infty)$ can be determined from the variation of the resonance amplitude or second moment. In accord with Shulman [16],assuming the additivity of the dipole-dipole and quadrupole contributions to the second moment, the invariance of the integral intensity for deformation and finally a Gaussian line form, one finds

$$\Delta\nu = \left\{ \frac{M_2^o}{S} \left(\frac{D_o}{D} - 1 \right) \right\}^{1/2} \qquad /12/$$

where M_2^o is the second moment in the undeformed lattice in the direction $<100>$, D_o and D the peak to peak derivative amplitudes without and with deformation respectively, s the relative satellite intensity.

It was found that within the experimental accuracy for amplitude measurement, $\sim$ 1 %, the amplitude of the derivative does not change with the deformation. This leads to an upper boundary for the satellite frequency shift: $\Delta\nu \leq 370$ Hz.

The parameter λ' can be determined from the point-ion model after summation for the first hundred coordination shells. In the present case on gets $\lambda' \leq 2{,}4$. Denoting by λ that value, which is obtained, when the first coordination shell is taken into account only /that quantity is to be directly compared with data in the literature/ one finds a limit $\lambda \leq 1{,}5$, in good agreement with the results of Faulkner, Averbuch et al and Ogurtani et al. It is of course plausible to multiply the existing data by the factor $K^{(1)}/K^{(100)} = 1{,}65$ for further references.

The Sholl theory as applied for homogeneously strained copper single crystal, gives the following limiting value for considering the first 1000 coordination shells: $(1 - \gamma_\infty) \leq 25$ which value, considering our suppositions about the unscreened potential and the neglect of directional scatter of the crystallites seems to be a reasonable one.

From the results of Averbuch et al $\lambda \sim 1,2$ the following estimate is obtained $(1 - \gamma_\infty) \sim 21$.

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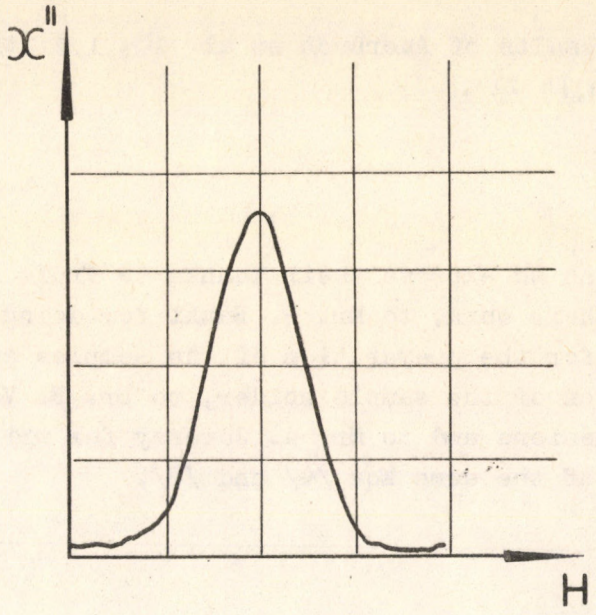

Fig. 1.

^{63}Cu NMR signal on foils of 40 mg effective mass

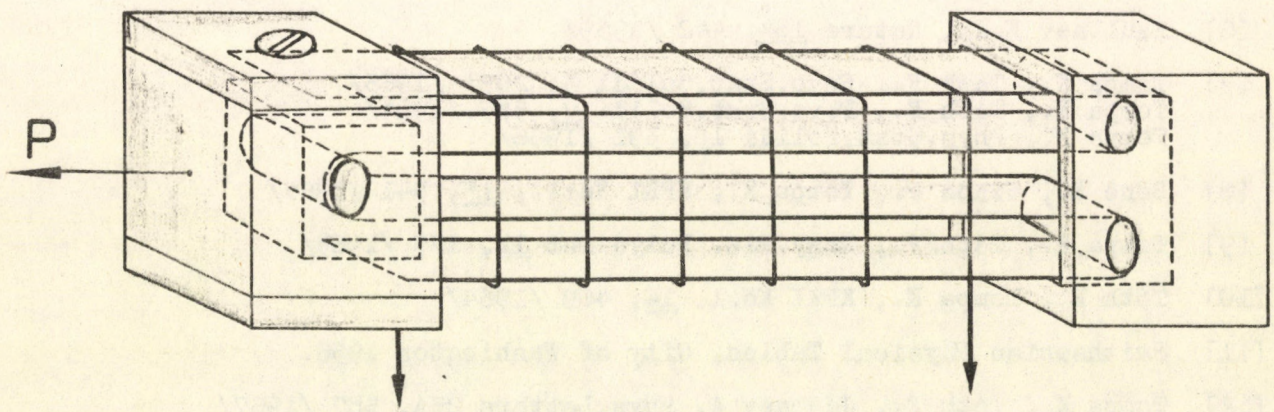

Fig. 2.

NMR measuring head for deformation measurements