SIZE EFFECT IN NUCLEAR MAGNETIC RESONANCE

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A broadening of the NMR line in fine particles of lead has been observed. This broadening appears to be understandable in terms of charge density fluctuations emanating from crystal surfaces. The effect is similar, therefore, to that described by Blandin et al.[1,2] wherein long-range charge density fluctuations around impurities in metals change the Knight shift and broaden the resonance line for the alloy.

We estimate the effect of introducing a surface by treating a semi-infinite medium and compute fluctuations, $\delta\rho(x, E_F)$, in the density of electrons per unit volume per unit energy evaluated at the Fermi energy, E_F. The computations are on the basis of a free-electron model, but, when normalized to the unperturbed density $\rho_0(x, E_F)$, the result is essentially the same as for Bloch electrons.[2] We then introduce a lattice of nuclei and compute the relative shift,

$$\delta_{\text{K.S.}} = \frac{\sum_i \delta\rho(x_i, E_F)}{\sum_i \rho_0(x_i, E_F)}, \quad (1)$$

and the mean-square deviation,

$$\Delta = \left\{ \frac{\sum_i |\delta\rho(x_i, E_F)|^2}{[\sum_i \rho_0(x_i, E_F)]^2} - \frac{|\sum_i \delta\rho(x_i, E_F)|^2}{[\sum_i \rho_0(x_i, E_F)]^2} \right\}^{1/2}, \quad (2)$$

of the density evaluated at the nuclei. The sums are over the lattice positions, x_i, and Δ is equal to the ratio of the extra breadth of the line to the absolute Knight shift.[2]

$\rho(x, E_F)$ may be seen to be equal to the charge density due to a single electron at the Fermi surface (averaged over the Fermi surface) times the density of states at the Fermi surface. For a semi-infinite medium we require the wave functions to vanish at the plane $x = 0$. Then the probability density due to a single electron will be proportional to $\sin^2 k_x x$, where k_x is the x component of the wave number. The average over the Fermi surface is proportional to $(1 - \sin 2k_F x/2k_F x)$. Thus,

$$\rho(x, E_F) = \rho_0(1 - \sin 2k_F x/2k_F x), \quad (3)$$

where ρ_0 is the electron density per unit volume

and energy at large distance; i.e., the unperturbed density. Thus

$$\delta\rho(x, E_F) = -\rho_0 \sin 2k_F x/2k_F x. \quad (4)$$

We now define a lattice to consist of planes of atoms at values of x given by a, $2a$, $3a$, $\cdots$. Thus in terms of this lattice our boundary condition is such that the wave functions vanish one lattice distance before the first atomic plane. Then

$$\sum_i \delta\rho(x_i, E_F) = -\rho_0 N_2 N_3 \sum_{n=1}^{N_1} \frac{\sin 2k_F an}{2k_F an}, \quad (5)$$

where N_1 is the number of atom planes over which the sum is taken and $N_2 N_3$ is the number of atoms per plane. The sum may be evaluated directly for the limit of N_1 large. We obtain

$$\delta_{\text{K.S.}} = \frac{\sum_i \delta\rho(x_i, E_F)}{\sum_i \rho_0} = \frac{-\pi - \langle 2k_F a \rangle}{4k_F L}, \quad (6)$$

where $L = N_1 a$ is the distance into the crystal to which the average is carried. $\langle y \rangle$ denotes the residue of y modulo 2π (i.e., the difference between y and the largest value of $2\pi p$ less than y, where p is an integer). Equation (6) is used to obtain the plot in Fig. 1.
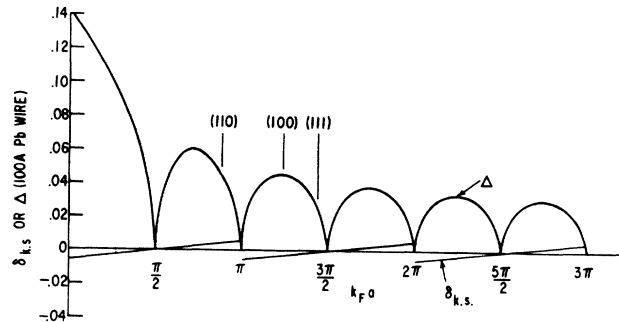
The broadening may also be computed in the

FIG. 1. Plot of the broadening and Knight-shift deviation parameters, Δ and $\delta_{\text{K.S.}}$, for a 100Å square lead wire as a function of the product of the Fermi wave number, k_F, and atom separation, a.

limit of N_1 large;

$$\sum_i |\delta\rho(x_i, E_F)|^2 \cong \rho_0^2 N_2 N_3 \sum_{n=1}^{\infty} \frac{\sin^2 2k_F an}{(2k_F an)^2}$$

$$= \frac{\rho_0^2 N_2 N_3}{(2k_F a)^2} [\tfrac{1}{2}\pi\langle 4k_F a\rangle - \tfrac{1}{4}\langle 4k_F a\rangle^2]. \quad (7)$$

We note under the square root in Eq. (2) that the second term is of order $(1/k_F L)^2$ whereas the first is of order $1/k_F L$ (since $k_F a$ is of order 1). Therefore we drop the second and obtain

$$\Delta \cong \frac{1}{2(k_F L)^{1/2}} \left[\frac{\pi\langle 4k_F a\rangle}{4k_F a} - \frac{\langle 4k_F a\rangle^2}{8k_F a}\right]^{1/2}. \quad (8)$$

For a square wire of dimension D, we add the squared fluctuations from four surfaces and obtain

$$\Delta_{wire} = \frac{1}{(k_F D)^{1/2}} \left[\frac{\pi\langle 4k_F a\rangle}{4k_F a} - \frac{\langle 4k_F a\rangle^2}{8k_F a}\right]^{1/2}. \quad (9)$$

For lead k_F is 1.58 Å^{-1}. The spacing of planes depends upon the crystallographic orientation of the surface; thus for (100), (110), and (111) crystal surfaces the values of $k_F a$ would be 3.89, 2.77, and 4.52, respectively. For a real crystal some average is appropriate.

Using the above values, Eq. (9) is evaluated for a 100Å square lead wire and plotted in Fig. 1. We see from this figure that the changes in Knight shift are sometimes positive and sometimes negative, and we therefore expect any shift to be quite small. The broadening, on the other hand, is much the same for each orientation; we will take the values for a wire with (100) surfaces for comparison with experiment.

Figures 2 and 3 illustrate electron micrographs of porous glasses which have been pressure-impregnated with lead metal. These glasses, which are of the phase-separable borosilicate variety, may be prepared with relatively closely sized connected pores. The characteristic pore diameters range from a few tens of angstroms to a few hundred angstroms depending on original glass composition and heat treatment. In the present case two porous glasses were chosen to obtain filaments of lead which were approximately 100 Å in diameter (Fig. 2) and about 300 Å (Fig. 3). Included in each of these figures are NMR differential absorption curves showing a fine
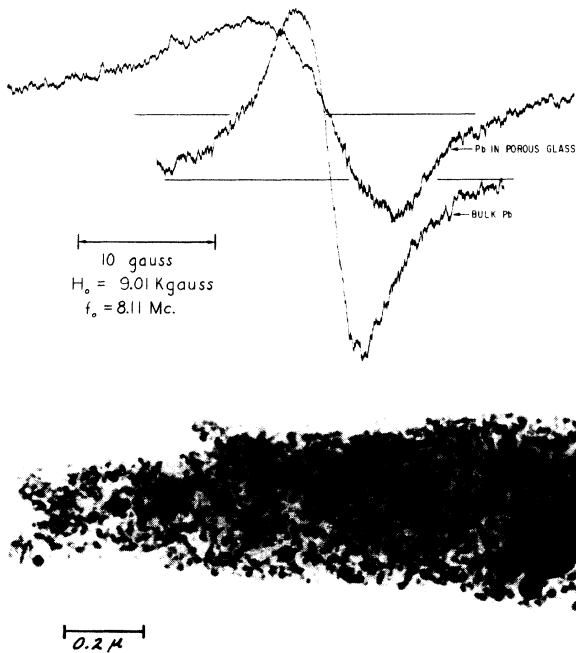

FIG. 2. Differential NMR absorption curves of Pb showing fine particle broadening. The transmission electron micrograph of a chip of the Pb-impregnated porous glass shows the Pb filaments to have a characteristic size of about 100 Å.
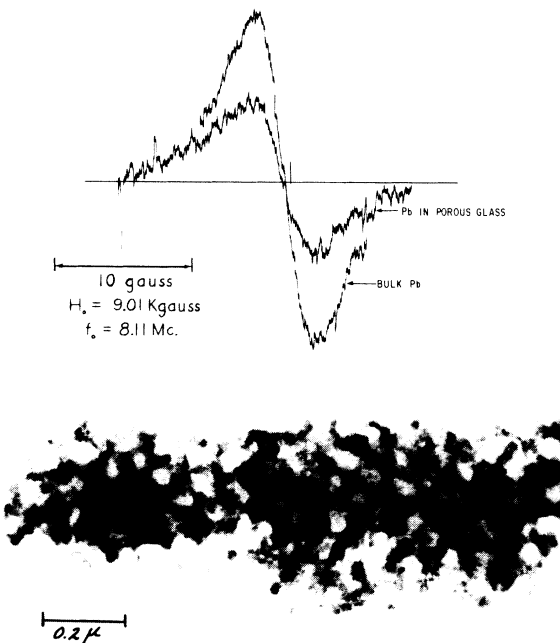

FIG. 3. Differential NMR absorption curves of Pb showing fine particle broadening. The transmission electron micrograph in this case shows the Pb filaments to have a characteristic size of about 300 Å.

Table I. Comparison of theory and experiment.

Sample	D (Å)	Linewidth δH (gauss)	Extra linewidth[a] $\Delta(\Delta H_0)$ (gauss)	Extra broadening Δ (meas)	(calc)
No. 1 (Pb in glass)	~100	10.3	9.4	0.071	0.045
No. 2 (Pb in glass)	~300	5.2	3.0	0.023	0.026
No. 3 (standard)	4×10^4	4.2	0	...	...

[a] $\Delta(\Delta H_0) = (\delta H^2 - \delta H^2_{standard})^{1/2}$.

particle resonance line superimposed upon a standard resonance line. The standard line, in each case, was obtained from an equivalent amount of large lead particles distributed over the same volume. Auxiliary measurements determined the natural line width of lead[3] to be 4.2 gauss and the Knight shift to be 1.47%.

Examination of the NMR traces indicates that if any deviation of the line position occurs it is too small to be observed. Such a result is in line with expectation. On the other hand, the line broadening is extensive and Table I compares the extra broadening estimated using Eq. (9) with that observed. The correspondence is satisfactory and lends support to the present description of the effect. It is seen that the measured values of Δ do not fully establish an inverse square root dependence on size. We attribute this lack of agreement to uncertainties in assigning characteristic sizes to the lead particles, particularly over the small range investigated.

Since the extra broadening of the resonance line is attributed to a distribution of Knight shifts it should exhibit a magnitude proportional to the field. Experiments at 12, 8, and 6 kG did, in fact, show the observed linewidth to decrease approximately as the ratios 1.7:1.2:1. These values give a roughly linear relationship between extra linewidth and field as required.

[1] A. Blandin, E. Daniel, and J. Friedel, Phil. Mag. 4, 180 (1959).

[2] A. Blandin and E. Daniel, J. Phys. Chem. Solids 13, 257 (1959).

[3] L. I. Piette and H. E. Weaver [J. Chem. Phys. 28, 735 (1958)] give the linewidth of lead as 2.6 gauss and the Knight shift as 1.4%. While we concur on the value of the shift, we are unable to account for the difference in the linewidths. The presently determined value is used for calculations in this work.

OPTICAL SYMMETRY OF THE SELF-ACTIVATED LUMINESCENCE CENTER IN ZnS SINGLE CRYSTAL

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In the investigation of the nature of luminescence centers, especially the symmetry thereof, the measurement of the polarization of luminescence is a very useful tool. The polarization of luminescence in ZnS type crystals was reported by some investigators.[1] However, the results obtained up to the present were all explained by attributing the polarization to the symmetry of the energy bands of the hexagonal host

lattice.[2] The polarization which correlates with the symmetry of the luminescence center itself as found in alkali halides[3] and diamond[4] has never been found in sulfide crystals. This is the first report that in ZnS type crystals the optical symmetry of the luminescence center has been revealed by the polarization characteristics, thereby presenting information about the nature of the radiative transition.
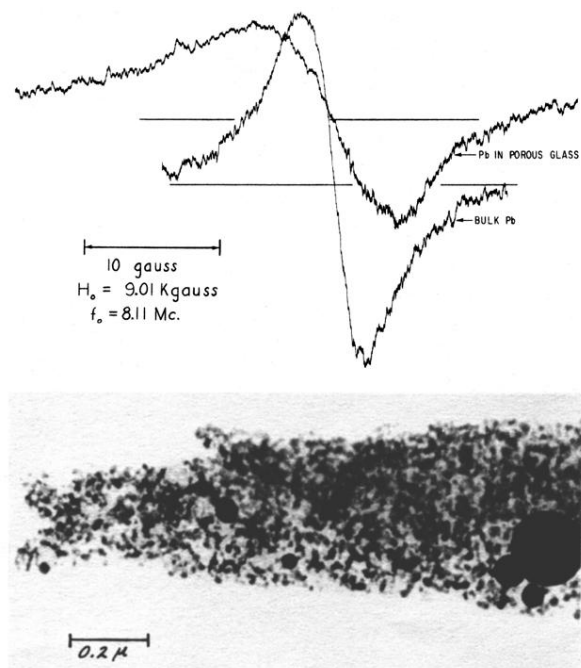
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10 gauss

H_o = 9.01 Kgauss

f_o = 8.11 Mc.

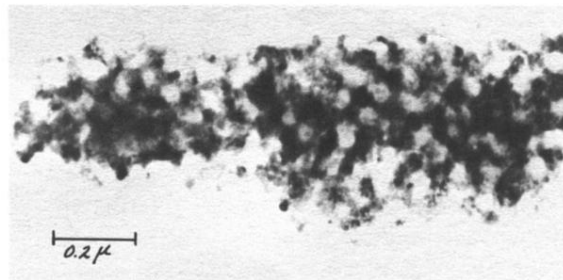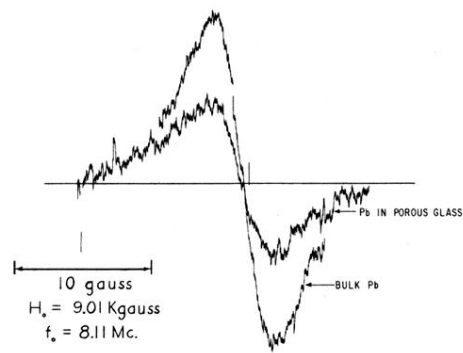Pb IN POROUS GLASS

BULK Pb

0.2 μ

FIG. 3. Differential NMR absorption curves of Pb showing fine particle broadening. The transmission electron micrograph in this case shows the Pb filaments to have a characteristic size of about 300 Å.