

limit of the percentage of diffused surface scattering from field effect data.

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<sup>1</sup>For a review of surface physics see Semiconductor Surface Physics, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957).

<sup>2</sup>J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).

<sup>3</sup>Bardeen, Coover, Morrison, Schrieffer, and Sun, Phys. Rev. **104**, 47 (1956).

<sup>4</sup>J. N. Zemel and R. L. Petritz, Phys. Rev. **110**, 1263 (1958).

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### DIAMAGNETIC NUCLEAR MAGNETIC RESONANCE SHIFTS IN ALLOYS

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We have observed large diamagnetic shifts of several nuclear magnetic resonances in alloys which have the  $\beta$ -wolfram structure. These shifts were as large as 0.62% and were observed in  $\text{Nb}_3\text{Sn}$ ,  $\text{V}_3\text{Sn}$ , and  $\text{V}_3\text{Ga}$  for the tin and gallium nuclei. However, no shifts of the gallium resonances in the isomorphous alloy  $\text{Nb}_3\text{Ga}$  were observed. In all four compounds, the resonances of two isotopes, i.e., either  $\text{Ga}^{69}$  and  $\text{Ga}^{71}$  or  $\text{Sn}^{117}$  and  $\text{Sn}^{119}$ , were observed and the fractional shifts were the same for either isotope of an element. All nuclei measured were in a body-centered cubic site of the  $\beta$ -wolfram cubic lattice in which they are surrounded by twelve equidistant near neighbors. Shifts observed are plotted versus temperature in Fig. 1. Most of the measurements were made at 16 Mc/sec but to within experimental accuracy the fractional shifts,  $\Delta H/H_0$ , were observed to be independent of the external magnetic field  $H_0$ . Samples were crushed and sieved through a 325-mesh screen so that all particles were  $< 4 \times 10^{-3}$  cm in diameter during the measurements reported. The resistivities of the samples are not known, hence the skin depth could not be calculated exactly. However, they are of higher resistivity than copper and  $4 \times 10^{-3}$  cm should be less than the skin depth.

The separations between derivative extrema were  $8.5 \pm 0.5$  gauss for the tin and gallium resonances in  $\text{V}_3\text{Sn}$  and  $\text{V}_3\text{Ga}$  while in the homolog-

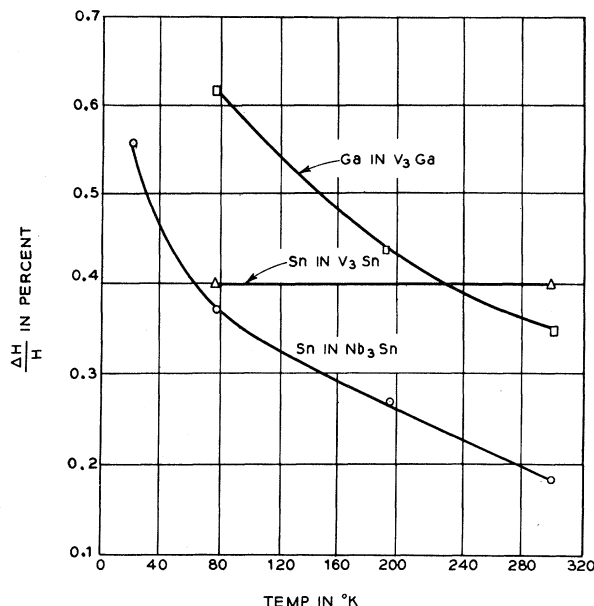


FIG. 1. Percentage diamagnetic shifts of the resonances as a function of temperature. Tin shifts were measured with respect to an aqueous solution of  $\text{SnCl}_2$ . Gallium shifts were measured from deuterium by assuming  $\gamma_D/\gamma_{H1} = 0.5034$ . The gallium resonances in  $\text{Nb}_3\text{Ga}$  were shifted less than 0.02%.

ous niobium alloys they were  $9.5 \pm 0.5$  gauss. All resonances were symmetrical. In most cases the signal/noise ratio did not permit a second-moment determination. However, these widths are close to what one expects from nuclear dipolar broadening alone.

In order to see if this large diamagnetic shift was present in other tin compounds, the  $\text{Sn}^{119}$  resonance was measured in four other tin compounds. All shifts were measured from the  $\text{Sn}^{119}$  resonance in a saturated water solution of  $\text{SnCl}_2$ . The displacements were  $\text{Sn}^{119}\text{O}_2$ ,  $+(0.03 \pm 0.01)\%$ ;  $\text{Sn}^{119}\text{O}$ ,  $+(0.06 \pm 0.01)\%$ ;  $\text{Sn}^{119}\text{S}$ ,  $< 0.01\%$ ; and  $\text{Sn}^{119}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ,  $< 0.01\%$ . The positive sign indicates a paramagnetic shift. The reference  $\text{Sn}^{119}$  resonance in solution was measured at constant field relative to  $\text{Li}^7$  in a saturated  $\text{LiCl}$  solution and the ratio obtained was  $g^{119}/g^7 = 0.95915 \pm 0.00005$ .

Since the band structure of these alloys is unknown, it is not possible to explain with any certainty the absence of a paramagnetic<sup>1</sup> Knight shift. Measurements by R. M. Bozorth of the  $\text{Nb}_3\text{Sn}$  susceptibility indicated a slight paramagnetic contribution, roughly temperature independent in the range of our measurements, so that bulk diamagnetism is not responsible for the shifts. The  $\beta$ -wolfram structure is particularly

conductive to high superconducting<sup>2</sup> transition temperatures. Correlation of these shifts with the superconducting potentialities is lost when one considers that the critical temperatures<sup>3</sup> are Nb<sub>3</sub>Sn, 18.05°K; V<sub>3</sub>Sn, 6°K; and V<sub>3</sub>Ga, 17°K; while for Nb<sub>3</sub>Ga, which showed no NMR shift, it is<sup>4</sup> 16.8°K. The mechanism responsible for these shifts is not presently understood.

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## THEORY OF GALVANOMAGNETIC EFFECT AT HIGH MAGNETIC FIELD

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According to the general theory of irreversible processes<sup>1</sup> the conductivity tensor is expressed as

$$\sigma_{\mu\nu} = \int_0^\infty dt \int_0^\beta d\lambda \langle j_\nu(-i\hbar\lambda) j_\mu(t) \rangle, \quad (1)$$

where  $\beta$  is  $1/kT$  and

$$j_\nu = \int \psi^\dagger v_\nu \psi d\vec{r} \quad (2)$$

is the current density operator,  $\psi^\dagger$  and  $\psi$  being quantized electron wave functions normalized per unit volume.  $v_\nu$  is the one-electron operator for the velocity. The average is taken over the equilibrium in the absence of the electric field. The best way of treating the electronic conduction in magnetic field is to start from this expression, because the transport equation of usual Boltzmann-Bloch type may not be used particularly in strong magnetic field, where the condition

$$\omega_0 \tau_r \gg 1 \quad (3)$$

is satisfied. Here  $\omega_0$  is a measure of cyclotron

frequencies and  $\tau_r$  that of the relaxation time. Under this condition, where electrons complete cyclotron cycles before they get scattered, and at low temperatures, the quantum-mechanical effect appears in transport properties as de Haas-van Alphen type oscillations and further as some asymptotic behaviors at extremely strong magnetic fields where only the lowest Landau levels are occupied (quantum limit).

Let us consider crystal electrons which are described by the energy function  $E_0(\vec{p})$  in the absence of magnetic field,  $\vec{p}$  being the crystal momentum. From general considerations, it is seen that the cyclotron motion may be represented by the set of canonical variables  $(\xi, \eta)$ ,  $(X, Y)$ , and  $(p_z, z)$  which satisfy the commutation rules

$$[\xi, \eta] = [Y, X] = l^2/i, \quad l^2 \equiv \hbar c/eH, \quad [p_z, z] = \hbar/i. \quad (4)$$

Here  $z$  is the Cartesian coordinate of an electron in the direction of the magnetic field.  $(\xi, \eta)$  may be called the relative coordinates and  $(X, Y)$  the center coordinates of cyclotron motion, because the Cartesian coordinates in the projection normal to the magnetic field are

$$x = X + \xi, \quad y = Y + \eta, \quad (5)$$

and  $(\xi, \eta)$  are defined by

$$\xi = (c/eH)\pi_y, \quad \eta = -(c/eH)\pi_x, \quad (6)$$

where

$$\pi_x = p_x + (e/c)A_x, \quad \pi_y = p_y + (e/c)A_y$$

are the noncommutative quasimomentum components in magnetic field.

The effective Hamiltonian of an electron is, if the interband effect is neglected, given by<sup>2</sup>

$$\mathcal{H} = E_0(\pi_x, \pi_y, p_z) + U(x, y, z),$$

where  $U$  is the scattering potential. The above introduced definitions and the Hamiltonian lead to the equation of motion,

$$\dot{X} = \frac{c}{eH} \frac{\partial U}{\partial y}, \quad \dot{Y} = -\frac{c}{eH} \frac{\partial U}{\partial x}, \quad (7)$$

which is valid both classically and quantum-mechanically. So  $X$  and  $Y$  are constant if  $U$  is zero, and therefore  $\xi$  and  $\eta$  define the cyclotron motion relative to the center  $(X, Y)$ . Consequently, the velocity in (2) is divided into two parts,

$$v_x = \dot{X} + \dot{\xi}, \quad v_y = \dot{Y} + \dot{\eta},$$

and the conductivity tensor, Eq. (1), will then consist of four components.