

FIG. 2. Schematic diagrams of the energy band contours in perfect Ge and Si crystals along [111] and [100] axes in the reduced zone as suggested by Herman.² The removal of the degeneracy by spin-orbit interaction is not shown.

sition. If the conduction band minima are a Δ_1 state in Si and an L_1 state in Ge, as suggested by Herman,² then perturbation theory about the minimum gives

$$E = \frac{\hbar^2}{2} \left(\frac{k_1^2}{m_l} + \frac{k_2^2 + k_3^2}{m_t} \right), \quad (1)$$

where for the Δ_1 , $\mathbf{k} = k(100)$, minimum:

$$\frac{m}{m_l} = 1 + \frac{2}{m} \sum_{l=\Delta_1} \frac{|\langle \Psi_{100}^0 | p_x | \Psi_{100}^l \rangle|^2}{E_0 - E_l}; \quad (2)$$

$$\frac{m}{m_t} = 1 + \frac{2}{m} \sum_{l=\Delta_5} \frac{|\langle \Psi_{100}^0 | p_y | \Psi_{100}^l \rangle|^2}{E_0 - E_l}. \quad (3)$$

For the L_1 , $\mathbf{k} = (\pi/a)(111)$, minimum:

$$\frac{m}{m_l} = 1 + \frac{2}{3m} \sum_{l=L_2'} \frac{|\langle \Psi_{111}^0 | p_x + p_y + p_z | \Psi_{111}^l \rangle|^2}{E_0 - E_l}; \quad (4)$$

$$\frac{m}{m_t} = 1 + \frac{2}{3m} \sum_{l=L_3'} \frac{|\langle \Psi_{111}^0 | p_x + \omega p_y + \omega^2 p_z | \Psi_{111}^l \rangle|^2}{E_0 - E_l}, \quad (5)$$

where $\omega^3 = 1$.

Herman's² explanation (Fig. 2) of the optical gap change observed by Johnson and Christian³ does not show a Δ_1 level in Si or an L_2' level in Ge sufficiently close to the conduction band minimum to have a profound effect on m_l . The data for holes on the Ge-rich

side indicate that the levels at $\mathbf{k} = 0$ are separating in an orderly fashion.

There was some suggestion in the results at 24,000 Mc/sec that alloy scattering processes may tend to mix the different ellipsoids together, producing less anisotropy in the observed electron mass parameter. Such an effect, if it exists, would be most effective under conditions of low resolution ($\omega\tau \approx 1$). Our present practice for crystal orientation involves certain resonance degeneracy checks *in situ*, and such a procedure does not work effectively when the resolution is poor.

We are indebted to Mr. Robert Behringer for assistance with the measurements and to Dr. F. Herman and Professor C. Kittel for discussion of the results.

* The work at Berkeley was assisted by the Office of Naval Research and the U. S. Signal Corps.

¹ Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

² F. Herman, Phys. Rev. **95**, 847 (1954).

³ E. R. Johnson and S. M. Christian, Phys. Rev. **95**, 660 (1954).

Rapid Passage Effects in Electron Spin Resonance

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RELAXATION effects which have been observed in electron spin resonance from F centers in alkali halides¹ and from donor states in silicon² are interpreted here in terms of the rapid passage theory of Bloch.³ The distinguishing feature of the two cases in which these effects have been observed is that the line broadening is of the inhomogeneous type,^{4,5} arising from hyperfine interaction.

In Fig. 1 we show the dispersion signal obtained at room temperature from a sample of LiF irradiated with

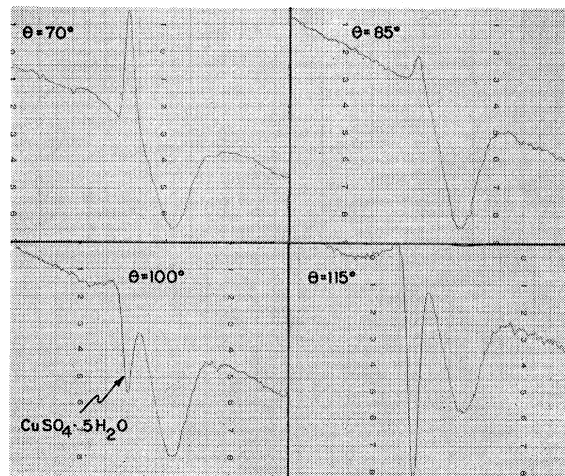


FIG. 1. Dispersion signal in LiF as a function of magnetic field for several values of θ , the phase angle between modulation field and reference signal.

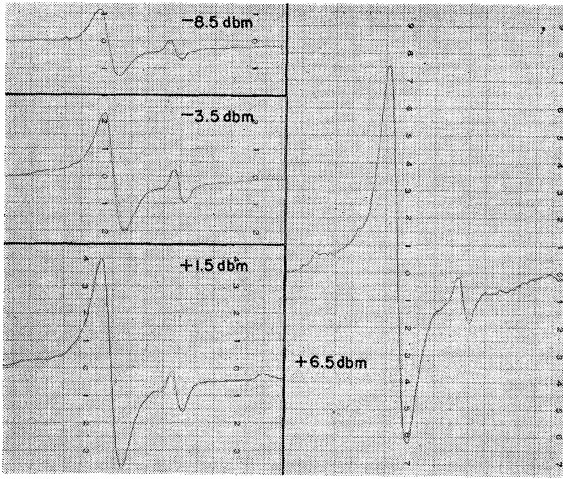


FIG. 2. Absorption signal in KCl as a function of magnetic field for several values of power incident on the microwave cavity. The low field signal is copper sulfate.

220-kev x-rays for a period of 18 hours. The signal is obtained by superimposing a small modulation field at a frequency of 280 cps on the static magnetic field and then detecting the component of the real part of the rf susceptibility which varies at this frequency. Two surprising results are evident from an examination of these curves:

1. The LiF signal lags the modulation field by nearly 90° .
2. The line shape of the LiF resonance more closely resembles an absorption curve than it does the derivative of a dispersion curve.

On the other hand, the copper sulfate signal appears quite normal. The difference between the primary sources of line broadening for these two samples suggests the reason for the difference in their behavior. It is well established that the source of the line width in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is magnetic dipolar broadening narrowed by exchange. The source of the line broadening in F centers is a hyperfine interaction.⁶ As has been suggested,⁴ it is appropriate to view the resonance from F centers as a series of resonances with a distribution given by the distribution in local hyperfine fields. In copper sulfate, resonance absorption must be associated with the electron spin system as a whole. Assuming that the line structure in LiF is as described one may ask whether, with an amplitude of magnetic field modulation comparable to the over-all line width, slow passage conditions can obtain.

Because of the large and almost continuous distribution in hyperfine fields and the dilution of the electron spin system, it is possible to use the Bloch equations and to assume that $T_2 = T_1$ as long as T_1 is not excessive. At low temperatures, where T_1 may be of the order of seconds, the situation is expected to be more complicated. Under saturation conditions the time of passage is of the order of $H_1/\omega_m H_m$, where $2H_1$ is the peak

transverse rf field and ω_m and H_m are the modulation frequency and field respectively. The recordings shown in Fig. 1 were taken with a time of passage of the order of 10^{-5} second. From saturation measurements we know that T_1 is longer than 10^{-4} second. Then, an individual resonance is traversed in less than one-tenth of a spin-lattice time. Bloch shows that under rapid passage the sense of the dispersion line reverses with the direction of travel and the intensity of the line is proportional to the value of S_z associated with the line. The observed phase shift of 90° and a line shape which reflects the local field distribution may be inferred directly from Bloch's results.

We have developed an expression for the deviation from the slow-passage rf susceptibility expressed as a power series in $\epsilon = \omega_m H_m T_1 / H_1$. We obtain for the component of the real part of the rf susceptibility periodic at the frequency of the modulation field:

$$\chi'(\omega) = \frac{1}{2} \pi \chi_0 \omega \left\{ - \frac{\partial}{\partial \omega_0} \int_0^\infty \frac{\omega' h(\omega', \omega_0) d\omega'}{\omega'^2 - \omega^2} \right\} \gamma H_m \cos(\omega_m t) + \frac{1}{4} \pi \chi_0 \omega \epsilon \cos \phi_1 h(\omega, \omega_0) \sin(\omega t - \phi_1) + O(\epsilon^3), \quad (1)$$

where $h(\omega, \omega_0)$ is the normalized distribution in local magnetic fields centered about the applied field, $H_0 = \omega_0 / \gamma$, and $\phi_1 = \tan^{-1}(\omega_m T_1)$. The first term on the right is simply the derivative of the dispersion envelope associated with the field distribution. The first-order correction introduces the field distribution itself, shifted in phase by nearly 90° .

In order to obtain an experimental check of Eq. (1) we have re-examined the electron resonance from F centers in KCl. Figure 2 shows the peculiar saturation behavior of the absorption which has already been discussed.⁴ From the data obtained we have determined that $T_1 = 5 \times 10^{-6}$ sec at room temperature. Then $\epsilon = 0.4$

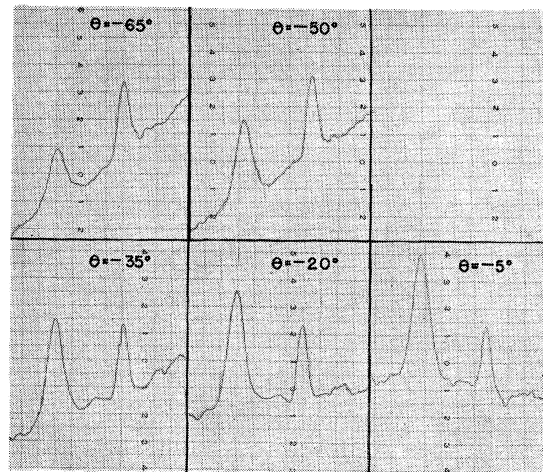


FIG. 3. Dispersion signal in KCl as a function of magnetic field for several values of θ , the phase angle between modulation field and reference signal. The low field signal is copper sulfate.

and at the line center, taking a shape of the form

$$h(\omega, \omega_0) = (T_2^*/\pi) \exp[-T_2^{*2}(\omega - \omega_0)^2/\pi],$$

we have

$$\chi'(\omega) = \frac{1}{2}(0.62)\chi_0\omega T_2^*(\gamma H_m T_2^*) \cos(\omega_m t) + \frac{1}{4}\chi_0\omega T_2^*\epsilon \sin(\omega_m t) + O(\epsilon^3). \quad (2)$$

The lag angle, $\phi = \tan^{-1}(0.81/\gamma H_m T_2^*) \sim 45^\circ$ for $\Delta H = 1/\gamma T_2^* = 19$ oersteds. In Fig. 3 we show the set of dispersion curves for KCl. The phase shift as determined from these curves is consistent with the above estimate. This confirms that rapid passage conditions are responsible for the observed effects.

It is a pleasure to thank Dr. F. Keffer for his interest in this work and Mr. D. Shaltiel for assisting with the preliminary measurements.

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¹ A preliminary account of the experimental work was given by A. M. Portis and D. Shaltiel, *Phys. Rev.* **98**, 264(A) (1955).

² A. F. Kip (private communication).

³ F. Bloch, *Phys. Rev.* **70**, 460 (1946).

⁴ A. M. Portis, *Phys. Rev.* **91**, 1071 (1953).

⁵ Fletcher, Yager, Pearson, and Merritt, *Phys. Rev.* **95**, 844 (1954).

⁶ Kip, Kittel, Levy, and Portis, *Phys. Rev.* **91**, 1066 (1953).

Phenomenological Equations for Superconductors

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IN every physical system at finite temperature the momenta of distant particles are uncorrelated—that is, there exists a “correlation length” Λ such that particles which are farther apart than Λ have rapidly decreasing momentum correlation.¹ Λ is very large in a lattice of particles; for nearly freely moving particles Λ is usually of the order of several mean free paths against collisions, although there are exceptional systems in which it can be much longer. No matter what the size of the correlation length, its very existence has important effects on the behavior of a system in temperature equilibrium when this system is rotated uniformly, or when it is put into a magnetic field.

It has been shown² that London’s equation,³

$$-\lambda c \operatorname{curl} \mathbf{j}_s = \mathbf{B}, \quad (1)$$

is incompatible with the existence of a finite correlation length; i.e., (1) implies an infinite correlation length (more precisely a correlation length proportional to the size of the container). This is illustrated by the fact that the only model known to obey Eq. (1), the ideal Bose-

Einstein gas of charged particles below its condensation point,⁴ does indeed have an infinite correlation length: the momenta of bosons occupying the ground state are correlated over the whole volume of the container.

It is therefore necessary to modify the London equation so as to be consistent with a finite correlation length Λ . This can be done by rewriting (1) in terms of the magnetization vector \mathbf{M} rather than the supercurrent density vector \mathbf{j}_s . The two vectors are related through

$$\mathbf{j}_s = c \operatorname{curl} \mathbf{M}, \quad (2)$$

so that Eq. (1) becomes

$$-\lambda c^2 \operatorname{curl} \operatorname{curl} \mathbf{M} = \mathbf{B}. \quad (3)$$

We now expand in an orthonormal set of vector eigenfunctions $\mathbf{u}_q(\mathbf{r})$ defined by

$$\operatorname{curl} \operatorname{curl} \mathbf{u}_q = q^2 \mathbf{u}_q, \quad (4a)$$

\mathbf{u}_q is normal to the surface of the superconductor, (4b) and

$$\int (\mathbf{u}_q)^2 d^3r = 1, \quad (4c)$$

where the last integral extends over the volume of the superconductor. These functions form a complete set. We write

$$\mathbf{M}(\mathbf{r}) = \sum_q M_q \mathbf{u}_q(\mathbf{r}), \quad \mathbf{B}(\mathbf{r}) = \sum_q B_q \mathbf{u}_q(\mathbf{r}). \quad (5)$$

Equation (3) becomes

$$M_q = -(\lambda c^2 q^2)^{-1} B_q. \quad (6)$$

In this form the equation can be modified. We introduce a “kernel” $K(q)$ which is a (so far unknown) continuous function of q , and write

$$M_q = -(\lambda c^2)^{-1} K(q) B_q. \quad (7)$$

The values of q which appear in (7) are the discrete eigenvalues of Eq. (4) for the particular shape and volume of the superconductor under study. The construction of Eq. (7) in terms of the eigenfunctions (4) ensures automatically that the supercurrent is parallel to the superconductor at its surface, provided only that $K(q)$ decreases sufficiently rapidly for large q .

It can be shown that, in terms of the kernel $K(q)$, the existence of a finite correlation length implies that the quantity $qK(q)$ must not become infinite as q approaches 0. Thus the London equation (6) gives an infinite correlation length. An additional clue to the form of $K(q)$ can be derived from the observed agreement between the London equation and the Meissner-Ochsenfeld effect. This indicates that $K(q)$ must behave like q^{-2} in the relevant region of q , i.e., for $q \sim d^{-1}$, where $d = c(\lambda/4\pi)^{1/2}$ is the London penetration depth. A simple kernel which satisfies both requirements is

$$K(q) = 1/[q(q+\mu)], \quad (8)$$

where μ is an inverse length, such that μ^{-1} is comparable

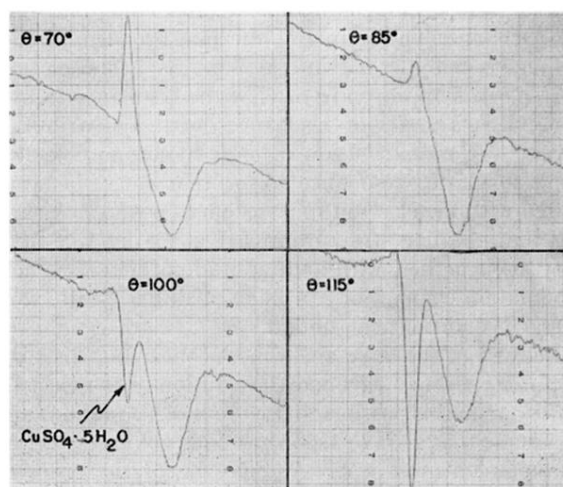


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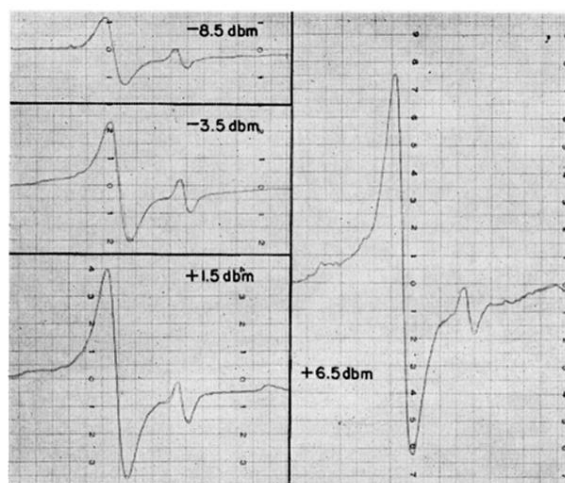


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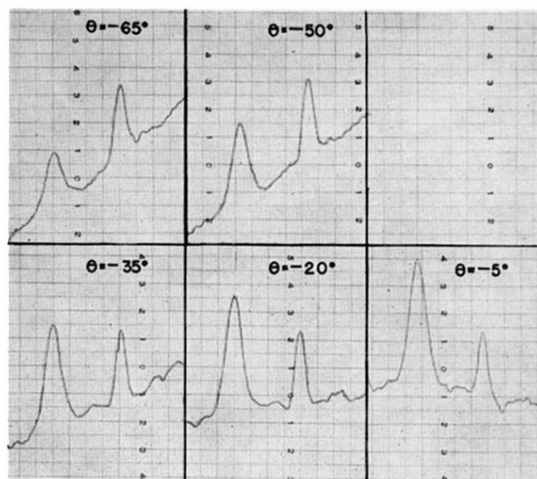


FIG. 3. Dispersion signal in KCl as a function of magnetic field for several values of θ , the phase angle between modulation field and reference signal. The low field signal is copper sulfate.