Paramagnetic Susceptibility in Superconductors*

Kei Yosida†

*Department of Physics,
University of California, Berkeley, California*
(Received March 4, 1958)

ACCORDING to Reif's experiment,[1] the Knight shift of superconducting colloidal mercury remains nonzero, about two-thirds of the normal value, at the absolute zero of temperature. This result seems difficult to understand on the basis of the Bardeen, Cooper, and Schrieffer theory of superconductivity[2] which is intimately connected to the energy gap at the Fermi surface. They suggested that a nonzero Knight shift might be accounted for by constructing collective excitations with no energy gap like spin waves in antiferromagnets. However, this would not be an easy thing to do as the excited states considered in the B.C.S. theory, all with an energy gap, form a complete set of excited states. On the other hand, Knight, Androes, and Hammond[3] reported that the second resonance absorption has been observed, near the proper frequency for a nonmetallic salt of Hg, in superconducting colloidal mercury under a different condition from Reif's experiment. The reason for the difference in these experiments is unknown, but clearly it would be of considerable interest to calculate the paramagnetic susceptibility by the B.C.S. theory.

Here we take the z axis as the quantization axis of conduction-electron spins, and assume that an external magnetic field is applied along the x axis. Then the Zeeman energy of the electron spin system is

$$H_z = 2\mu H \sum_i S_{ix}, \tag{1}$$

where μ is the Bohr magneton, H is the external magnetic field and S_{ix} is the x component of the spin of the ith electron. With the use of the same notations as in the B.C.S. theory, this can be expressed in a form of second quantization as

$$H_z = \mu H \sum_k (C_{k\uparrow}{}^* C_{k\downarrow} + C_{k\downarrow}{}^* C_{k\uparrow}). \tag{2}$$

(1) and (2) have only off-diagonal elements and the change of energy due to an external field comes from the second or higher perturbed energy for the non-degenerate ground state. Since it is easily shown that this energy change is, to second order in H, equal to the change of free energy for the paramagnetic susceptibility, we have only to calculate the second order perturbed energy of (2).

If we regard (2) as

$$H_z = \mu H \sum_k [C_{-k'\downarrow}{}^* C_{k\uparrow} + C_{k\uparrow}{}^* C_{-k'\downarrow}]_{k'=-k}, \tag{3}$$

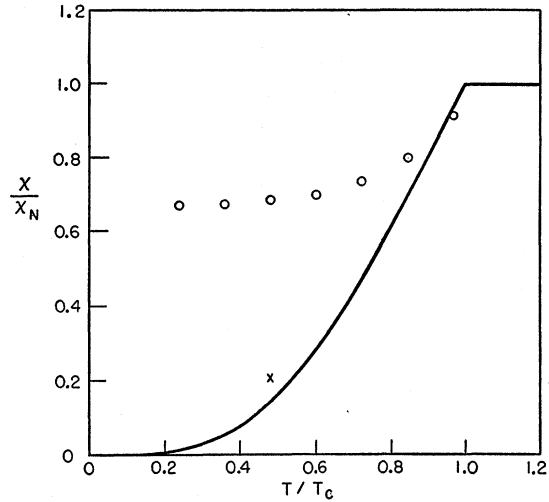we can easily calculate the second order perturbed

Fig. 1. Temperature dependence of the paramagnetic susceptibility of a superconductor. The circles represent experimental values by Reif,[1] the cross an experimental value by Knight *et al.*[3] (Knight *et al.* reported that at $T < 2°K$ a metallic shift is less than 0.5%. The cross in this figure corresponds to a shift of 0.5% at $T = 2°K$.)

energy E_2 with the help of Tables II and III in B.C.S. Thus we obtain

$$E_2 = -\mu^2 H^2 \sum_k L(\epsilon, \epsilon')_{\epsilon=\epsilon'}, \tag{4}$$

where $L(\epsilon, \epsilon')$ is given by (4.22) of B.C.S. with a lower sign. Putting $\epsilon = \epsilon'$, the first term of $L(\epsilon, \epsilon')$ becomes $-\partial f/\partial E$ and the second vanishes. Replacing the summation with an integration, we obtain

$$E_2 = -\frac{3N}{2E_F}\mu^2 H^2 \int_0^\infty dy \frac{\exp[(y^2+\beta^2\epsilon_0^2)^{\frac{1}{2}}]}{\{\exp[(y^2+\beta^2\epsilon_0^2)^{\frac{1}{2}}]+1\}^2}, \tag{5}$$

and the paramagnetic susceptibility

$$\frac{\chi}{\chi_N} = 2 \int_0^\infty dy \frac{\exp[(y^2+\beta^2\epsilon_0^2)^{\frac{1}{2}}]}{\{\exp[(y^2+\beta^2\epsilon_0^2)^{\frac{1}{2}}]+1\}^2}, \tag{6}$$

where β is $1/kT$, $2\epsilon_0$ the energy gap, N the total number of electrons, and E_F the Fermi energy. χ_N represents the normal value, namely $(3N/2E_F)\mu^2$. The right-hand side of (6) becomes unity as ϵ_0 vanishes. Thus the paramagnetic susceptibility decreases from the normal value at the transition temperature T_c with decreasing temperature and vanishes exponentially at $T = 0°K$. As has been shown in Appendix C of B.C.S., (6) is expressed in terms of β and ϵ_0 as

$$\frac{\chi}{\chi_N} = \frac{\beta}{\epsilon_0}\frac{d\epsilon_0}{d\beta} \Big/ \left(1 + \frac{\beta}{\epsilon_0}\frac{d\epsilon_0}{d\beta}\right). \tag{7}$$

The temperature dependence of χ/χ_N calculated from (7) is shown in Fig. 1 together with the experimental values by Reif[1] and Knight et al. It is very interesting to note that the experimental value obtained by Knight et al.[3] is very close to the theoretical curve. It seems likely that if a more refined theory were used to construct collective excitations with no energy gap, like spin waves in antiferromagnets, that the exponential decrease of χ with temperature would be replaced by a decrease like T^n where n is some positive power; but it seems very unlikely that such a refinement would give rise to a nonzero value for χ at zero temperature. We therefore conclude that the theory is in rough agreement with the experimental results of Knight et al. but in disagreement with those of Reif.

I am very much indebted to Professor C. Kittel, Professor M. Tinkham, and Dr. W. Marshall for their invaluable discussions.

[1] F. Reif, Phys. Rev. 106, 208 (1957).
[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957). We shall call this B.C.S. hereafter.
[3] Knight, Androes, and Hammond, Phys. Rev. 104, 852 (1956).

Acoustical Loss and Young's Modulus of Yttrium Iron Garnet

D. F. GIBBONS AND V. G. CHIRBA

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received February 17, 1958)

YTTRIUM iron garnet and other rare earth garnets are important as a new class of magnetic oxides. The yttrium iron garnet crystal structure has cubic symmetry with the magnetic ions occupying octa- and tetrahedrally coordinated positions in the lattice, as is the case in ferrites (ferrites have similar but not identical crystal structure). Because of the variety of stress-induced relaxations which have been reported in ferrites[1,2] and the anomalous peak in the ferrimagnetic resonance line width between 20–65°K,[3] Young's modulus and acoustical attenuation of polycrystalline yttrium iron garnet were measured by a technique which has been described elsewhere.[4]

Two samples[5] were prepared by sintering the oxides at 1450°C in O_2. The first sample contained some alumina and silica as impurities, and the variation of Young's modulus and attenuation (Q^{-1}) with temperature is shown in Fig. 1. There is a typical stress-induced relaxation at 153°K for a frequency of 84.8 kc sec^{-1}.
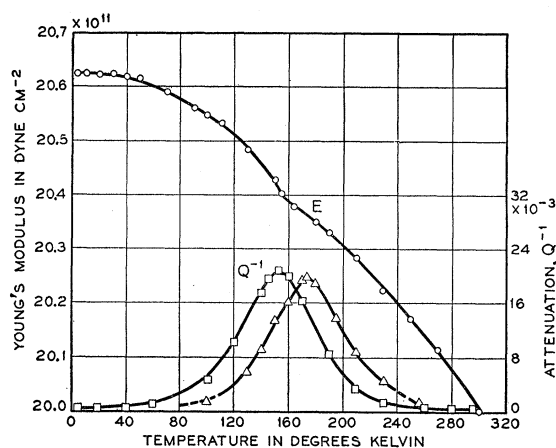

FIG. 1. Young's modulus and attenuation (Q^{-1}) for sample of yttrium iron garnet. □ attenuation at 84.8 kc sec^{-1}; △ attenuation at 249.2 kc sec^{-1}.

By exciting the specimen at its third harmonic, the maximum in the attenuation is shifted to 172°K. The shift corresponds to an activation energy of 0.12 ev/unit process. (A simple Arrhenius relation was used to calculate the activation energy even though the half-peak width is too broad for it to be strictly applicable.) A second specimen, prepared by a more refined technique, contained total impurities <0.05% and was within ±0.05% of the stoichiometric composition $Y_3Fe_2(FeO_4)_3$. The stress-induced relaxation was only just resolvable with a maximum attenuation of 2.0 $\times 10^{-4}$, an order of magnitude less than the first sample. The activation energy was the same as for the first sample.

Spheres of 0.010-in. diameter were made from each of the samples and the ferrimagnetic line width at 16 kMc sec^{-1} was measured at room temperature. The line width of the first sample was 150 oersteds while that of the second sample was only 47 oersteds. These observations lead us to believe that the stress-induced relaxation is not present in a homogeneous stoichiometric garnet structure. Localized departures from stoichiometry, however, allow the existence of a defect structure which is coherent (that is, not present as a second phase) with the parent garnet matrix. In this case, a stress-induced relaxation could occur by the stress-induced migration of electrons or ions. The value of the observed activation energy is lower than would be expected from an ion migration and is more in favor of an electron migration, indicating incomplete oxidation of the metal ions in the neighborhood of the defects. Because of the similarity between this relaxation peak and those reported in manganese ferrite crystals[1] and hausmannite[6] (i.e., the broad relaxation peak and variation of the peak with purity and homogeneity), it is felt that these relaxations are not a property of the stoichiometric defect-free composi-