are present in fcc transition metals; they are remarkably strong, fairly independent of the parameters, and located in an energy range easily accessible to experimental verification, assuming that the difficulties inherent in studying well-characterized planar defects could be overcome.

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Measurement of the Superconducting Order-Parameter Relaxation Time from Harmonic Generation*

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The measured third harmonic power output from a paramagnetically doped superconductor in a stron microwave field has been found to vary with temperature as $(1-t)^{-1}$, as predicted by Gor'kov and Eliashberg's theory for concentrations close to critical and Eliashberg's theory for the dilute alloy. The magnitude of the order-parameter relaxation time deduced from the measured power is consistent with a model constructed from these two theories.

There is currently much interest in the relaxation times describing the return to equilibrium of superconductors disturbed in various ways. We report here the measurement of the relaxation time of the superconducting order parameter by a method that has not been used previously. It is also the first measurement of the relaxation time in the gapless superconducting state below T_c.

The experiment involves observing the third harmonic microwave response. It was carried out on a paramagnetically doped superconductor in order to test the validity of the theory of Gor'kov and Eliashberg[1] (GE) as well as to determine the magnitude of the order-parameter relaxation time appearing in the time-dependent Ginzburg-Landau (TDGL) equation that emerges from the theory.

In contrast to most of the methods used in many prior measurements of the diverse relaxation times in superconductors,[2-8] the harmonic generation technique offers the following advantages: freedom from geometry-dependent corrections, only slight disturbance from equilibrium, and direct indication of whether or not the order parameter Δ is following the rapidly varying electromagnetic field adiabatically.

The GE theory deals with superconductors containing a large enough concentration of magnetic impurities to destroy the energy gap at $T=0$, i.e., so that $\tau_s T_c(\tau_s) \ll 1$ or $T_c(\tau_s) \ll T_c(\infty)$, where τ_s is the average time between the reversals of the spin of a conduction electron due to scattering by the magnetic impurities, $T_c(\tau_s)$ and $T_c(\infty)$ are the transition temperatures of the doped and the pure superconductor, respectively. (Throughout we take $\hbar = k = c = 1$.) For such a superconductor in a sinusoidally oscillating magnetic field of frequency ω and amplitude H_ω, the theory predicts a depression of the order parameter that varies periodically at frequency 2ω. The amplitude of the Fourier component at 2ω is given by $\Delta_{2\omega} \propto (1 - 2i\omega\tau_R)^{-1}$, where $\tau_R = 3/\Delta_e^2\tau_s$, $\Delta_e^2 = 2\pi^2 T_c^2(1-t^2)$, $t = T/T_c$, and $T_c = T_c(\tau_s)$. Δ_e is the equilibrium value of Δ for $H=0$. The order parameter relaxation time τ_R is thus of the form $\tau_R = \tau_0/(1-t^2)$, where $\tau_0 = \frac{3}{2}\pi^2\tau_s T_c^2$. The time variations of Δ result in third-harmonic power generation through their effect on the supercurrent $\vec{J}_s \propto |\Delta|^2 \vec{A}$, where $\vec{A}$ is the vector potential.

In the experiment, the sample is placed in a dual-mode microwave cavity with resonant frequencies at ω and 3ω. At critical coupling, the third-harmonic output power is[9]

$$P_{3\omega} = \gamma\omega S^2 Q G^2/16\pi V |k_{3\omega}|^2,$$

where S is the sample surface area, Q is the loaded cavity quality factor, V is the cavity volume, and γ is a constant of order unity appropriate to the particular cavity mode. $k_{3\omega}$ is the propagation constant at 3ω within the superconductor. It is given by[10] $k_{3\omega}^2 = (-2i\delta_{sk}^{-2} + \delta_L^{-2})$, where $\delta_{sk} = \delta_{sk}(3\omega)$ is the normal state skin depth and $\delta_L = \delta_L(T)$ is the static field (London) penetration depth. G is the amplitude of the third-harmonic field in the ideal cavity[11] considered by GE. Explicitly,[12]

$$G = \frac{H_\omega^3}{2H_c^2}\left|\left(3 + \frac{k_{3\omega}}{k_\omega}\right)(k_\omega\delta_L)^4(1 - 2i\omega\tau_R)\right|^{-1},$$

where the thermodynamic critical field[13] $H_c = H_c(T) = (1-t^2)H_c(0)$. In the GE theory a single characteristic frequency, $\omega_R = \tau_R^{-1}$, governs both the nonlinear and linear behavior of the superconductor. ω_R is the "cutoff frequency" for the adiabatic response of Δ, and also marks the point at which the normal skin depth $\delta_{sk}(\omega) = \delta_L(T)$. The solid curves in Fig. 1 show the predicted output power versus the temperature for three values of $\omega\tau_0$.

The alloy system investigated was $La_{1-x}Gd_xSn_3$. This is close to being an ideal Abrikosov-Gor'kov system,[13] and has the advantages of high T_c (~ 6.45 K for $x=0$),[14] slow oxidation rate, and possibility

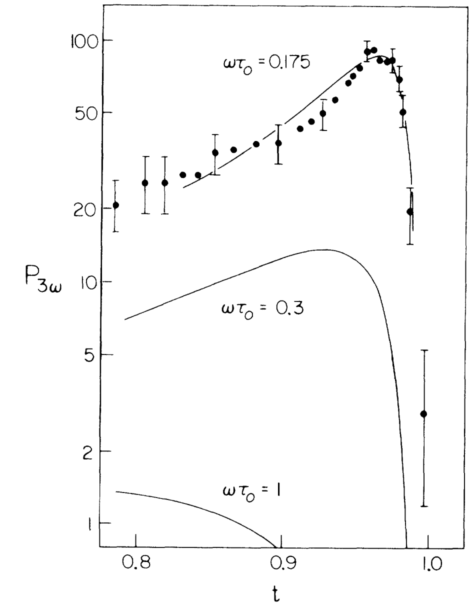

FIG. 1. Third harmonic power output $P_{3\omega}$ in arbitrary units versus $t = T/T_c(\tau_s)$. Solid curves: GE theory for different τ_0. The value $\omega\tau_0 = 0.175$ fits best to the experimental results for $La_{0.9}Gd_{0.1}Sn_3$, represented by the points.

for electropolishing.[15] The last two considerations were particularly important for microwave work.

Samples were prepared in a standard arc furnace using $6N$ tin and $4N$ rare-earth materials. After melting, the sample button was arc cast into cylindrical form, cut, and electropolished to a mirror-bright finish. The specimen was then spark-cut into three wafers, one of which was immediately transferred to the microwave cavity and cooled. The remaining two pieces were stored under xylene for low frequency T_c measurements on the following day. Separate samples were necessary for each measurement, since temperature-cycling promotes the precipitation of a tin-rich phase.[16] The sample surface was also examined by electron microscopy, using x-ray fluorescence to detect any compositional changes at the grain boundaries. No such changes were found.

Microwave measurements were made with a superheterodyne detector operating at $3\omega = 33$ GHz. The local oscillator was phase-locked to the third-harmonic of the 11-GHz source, allowing phase-sensitive detection at the intermediate frequency. In-phase and quadrature components of the signal were detected separately in order to extract the signal voltage from the background.

TABLE I. Inductive transition temperatures T_c and widths ΔT_c at 700 Hz (bulk) and 10 MHz (surface) for $La_{1-x}Gd_xSn_3$ alloys.

x	0.10	0.08
T_c (700 Hz)	3.06	3.98 K
ΔT_c (700 Hz)	0.16	0.12
T_c (10 MHz)	3.00	3.84
ΔT_c (10 MHz)	< 0.15	< 0.20

The measured system sensitivity was $\sim 10^{-18}$ W.

The sample formed part of the center conductor of a cylindrical coaxial cavity resonating in the $TE_{011}-TE_{01n}$ modes, and was electrically insulated from the surrounding cavity pieces by thin Mylar spacers. In order to avoid excessive sample heating, the input power was reduced to 10 mW, corresponding to a field amplitude $H_\omega \sim 0.2$ Oe at the specimen surface.

In addition to qualitative studies on many samples, we have carefully measured the third-harmonic power from two high quality samples with $x = 0.10$ and 0.08. The low frequency T_c data are summarized in Table I. Mutual inductance and skin depth measurements were made at 700 MHz, respectively, in order to measure the bulk and surface properties separately. Table I indicates that the transitions of these two samples were quite sharp, and that their surfaces did not differ significantly from the bulk.

Microwave data for one of these samples are shown in Fig. 1. The data for the other are similar but with slightly more scatter. A fit to the GE theory is shown, using the height of the curve as an adjustable parameter. For each sample a *sharp* transition was assumed on the following bases: the absence of any coarse concentration inhomogeneities in the electron microscope scans, the spreads of the transitions given in Table I, and the steepness of the slope at T_c of the observed $P_{3\omega}$ versus temperature graph, as shown by the points in Fig. 1. Comparisons of the latter curve with theoretical curves into which a Gaussian distribution of T_c had been folded indicated $\Delta T_c < 0.05$ K. Agreement with the theoretical temperature dependence is quite good for $t > 0.9$, although for lower temperatures the power output is higher than predicted. However, as shown in Table II, the experimental values of the constant τ_0 are about an order of magnitude larger than predicted by the GE expression $\tau_0 = 3/(2\pi^2\tau_s T_c^2)$, where τ_s is obtained from the Abrikosov-Gor'kov expression[13] for $T_c(\tau_s)$.

TABLE II. Experimental and theoretical relaxation times for $La_{1-x}Gd_xSn_3$ alloys, where $\tau_R(t) = \tau_0/(1-t^2)$.

x	0.10	0.08
τ_0 (exp)	$(2.5 \pm 0.4)\times 10^{-12}$	$(1.5 \pm 0.4)\times 10^{-12}$ sec
τ_0 (GE)	4.3×10^{-13}	1.9×10^{-13}

It is not surprising to find disagreement with the GE theory, since the theory assumes $\tau_s T_c \ll 1$, whereas for practical reasons the alloys studied in this experiment had $\tau_s T_c \sim 1$. (Attempts to produce higher concentration alloys result in precipitation of gadolinium.) For dilute alloys, with $\tau_s T_c \gg 1$, Eliashberg[17] has shown that the simple TDGL equation is replaced by two coupled differential equations. Instead of one characteristic frequency $\omega_R = \tau_R^{-1}$, there are now two. The condition $\delta_{sk} = \delta_L$ occurs at ω_1, which is the same order of magnitude as ω_R, but the adiabatic response of Δ now falls off at a different frequency $\omega_2 \ll \omega_1$. The greater complexity of the dilute limit arises because the diffusion process of pure superconductors displaces the homogeneous spin-flip pair-breaking process that dominates the order parameter relaxation mechanism in the concentrated limit.

Since neither of these limits is applicable to the present experiment and there is as yet no theory dealing with the case $\tau_s T_c \sim 1$, we have constructed from the GE and Eliashberg limits a hybrid model, which we use to further analyze the data of Fig. 1. In the spirit of the Eliashberg theory, we assume that the electromagnetic behavior is goverened by two characteristic frequencies, $\omega_1' = \omega_R$ and $\omega_2' \ll \omega_1'$. (The choice of $\omega_1' = \omega_1$ would not significantly change the analysis.) From the expressions given above for $P_{3\omega}$ and G, it can be seen that in the GE theory $P_{3\omega} = D/(1+4\omega^2\tau_R^2)$. D depends only on the thermodynamic and linear-response parameters (H_c, δ_L, k_ω, $k_{3\omega}$), while the denominator comes from the nonlinear behavior, i.e., the driven oscillations of the order parameter. The same is true of Eliashberg's theory in the limit of large values of the Ginzburg-Landau parameter κ, except that τ_R must be replaced by $\tau_2 = \omega_2^{-1} = \kappa^2\nu\omega_1^{-1}$, where $\nu = \pi^3\tau_s T_c/14\zeta(3) = 1.24 \times \tau_s T_c$. We assume that a similar factorization is also valid here and so write $P_{3\omega} = D/(1+4\omega^2\tau_2'^2)$. For $\omega\tau_2' \gg 1$, $D/P_{3\omega} = 4\omega^2\tau_2'^2$. The observed values of $P_{3\omega}$ have been combined with the calculated[13] temperature dependence of D to obtain τ_2' at different temperatures.

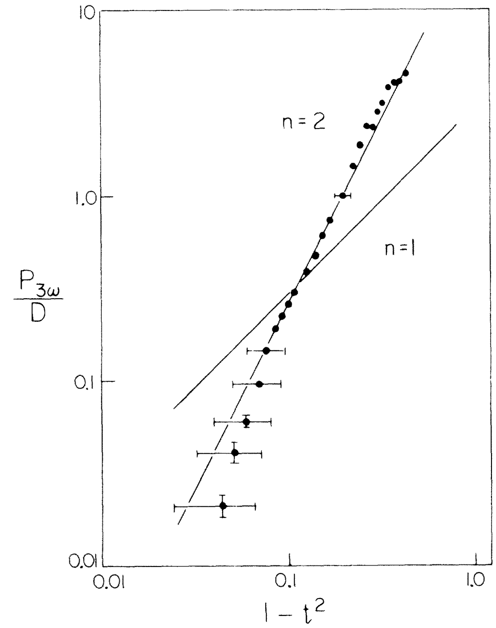

FIG. 2. $P_{3\omega}/D$ versus $(1-t^2)$. Assuming $P_{3\omega}/D \propto (1+4\omega^2\tau_2'^2)^{-1}$, and $\omega\tau_2' \gg 1$, then slope yields the exponent n in the relation $\tau_2' \propto (1-t^2)^{-n/2}$.

Anticipating $\tau_2'^2 \propto (1-t^2)^{-n}$, we have plotted $\ln(P_{3\omega}/D)$ versus $\ln(1-t^2)$ as shown in Fig. 2 for the $x = 0.010$ sample. Note the striking agreement with the value $n = 2$ (the large error bars on the lower points are due to the uncertainty in T_c), which indicates that the order-parameter relaxation time varies as $(1-t^2)^{-1}$, i.e., as $(1-t)^{-1}$ for $t \sim 1$. This is the form predicted by the GE theory and also the high κ limit of Eliashberg's theory. However, it is in contrast to the inverse square root dependence, i.e., $\tau \propto (1-t)^{-1/2}$, found in most cases[2-7] in the various relaxation times in superconductors with energy gaps. The one exception is in the recent experiment of Schuller and Gray[8] in which the relaxation time was found to vary as $(1-t)^{-1}$.

The Eliashberg theory also indicates why the experimental values of τ_0 in Table II are greater than expected from the GE theory. The values of the Ginzburg-Landau parameter κ for our specimens are estimated to be much greater than one, in which case the theory predicts $\tau_2/\tau_R \sim \omega_1/\omega_2 = \kappa^2\nu \gg 1$. In the absence of an accurate knowledge of the values of κ for our specimens, a more quantitative comparison of the theoretical and observed values of τ_0 is not warranted.

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