Femtosecond Room-Temperature Measurement of the Electron-Phonon Coupling Constant λ in Metallic Superconductors

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We report the first systematic femtosecond pump-probe measurements of the electron-phonon coupling constant λ in thin films of Cu, Au, Cr, Ti, W, Nb, V, Pb, NbN, and V_3Ga. The agreement between our measured λ values and those obtained by other techniques is excellent, thus confirming recent theoretical predictions of Allen. By depositing thin Cu overlayers when necessary, we can extend this technique to nearly any metallic thin film.

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In 1987, Allen[1] proposed that the electron-phonon coupling constant λ used in the Eliashberg generalization of BCS theory[2] might be measured using femtosecond (pump-probe) spectroscopy. Similar experiments have previously been performed in Cu (Ref. 3) and Au (Ref. 4). In these experiments, an ultrafast (<100 fs) pump pulse of light from a mode-locked laser heats the electron gas in the metal. For very short times (<1 ps), the electrons are thrown out of equilibrium with the host lattice, since the phonon emission rate is not large enough to maintain equilibrium. Thus, the electron temperature rises far above that of the lattice. Subsequent to the excitation, the electrons lose energy to the lattice via phonon emission; the electron and lattice temperatures equilibrate at a rate governed by the strength of the electron-phonon coupling. Thus, measuring the relaxation rate gives λ. The relaxation process can be monitored in time by delaying the probe pulse with respect to the pump. Herein, we report the first systematic measurement of λ in a variety of elements and alloys using pump-probe spectroscopy.

Using standard scattering rate formulas,[5] Allen was able to relate the relaxation rate of electron temperature T_e to $\lambda\langle\omega^2\rangle$ as[1]

$$T_e\frac{\partial T_e}{\partial t}\simeq-\frac{3\hbar}{\pi k_B}\lambda\langle\omega^2\rangle(T_e-T_l)\,, \tag{1}$$

where T_l is the lattice temperature, and $\langle\omega^2\rangle$ is the second moment of the phonon spectrum defined by McMillian.[2] Equation (1) assumes that the energy deposited in the sample by the pump pulse is distributed uniformly, so that we may neglect the effects of heat transport. In this case, T_e and T_l are related by[6]

$$C_e(T_e)\frac{dT_e}{dt}=-g(T_e-T_l)\,, \tag{2a}$$

$$C_l\frac{dT_l}{dt}=g(T_e-T_l)\,, \tag{2b}$$

where C_l is the lattice specific heat (constant at 300 K), and $C_e=\gamma T_e$ is the electronic specific heat. Comparison of (1) and (2a) shows that the coupling constant $g=3\hbar\times\gamma\lambda\langle\omega^2\rangle/\pi k_B$. Combining (2a) and (2b) leads to a nonlinear differential equation for T_e,

$$T_e\frac{d^2T_e}{dt^2}+\left(\frac{dT_e}{dt}\right)^2+\frac{3\hbar}{\pi k_B}\lambda\langle\omega^2\rangle\left(1+\frac{\gamma}{C_l}T_e\right)\frac{dT_e}{dt}=0\,, \tag{3}$$

which may be solved analytically given initial and final electron temperatures $T_e(0)$ and $T_e(\infty)$. All information needed to solve (3) are physical constants except the boundary values $T_e(0)$ and $T_e(\infty)$. These may be obtained from the laser-pulse energy and published metallic heat-capacity data. Thus, knowing T_e versus delay time t determines $\lambda\langle\omega^2\rangle$ with *no free parameters*.

The measurements are performed using a standard pump-probe setup;[7] the signal of interest is the change in intensity of the reflected probe beam ΔR as a function of time delay t after the arrival of the pump pulse. All measurements were done at room temperature. The laser source is a balanced colliding-pulse mode-locked dye laser[8] producing 60-fs pulses at a repetition rate of ~100 MHz. The average output power is 10 mW. The wavelength is 630 nm, corresponding to a photon energy of $\hbar\omega\simeq1.98$ eV. The pump beam is chopped to enable lock-in detection. The polarization of the probe beam is rotated to be orthogonal to the pump beam, so that stray light from the pump beam may be rejected using polarizers before detection. Both beams are focused on the sample with a microscope objective. Silicon photodiodes are used to monitor the reflected beam. After amplification, the $\Delta R(t)$ signal is detected using a lock-in amplifier and stored on a computer to facilitate the numerical fits.

For this technique to work, changes in T_e must cause R, the reflectivity of the sample at our laser energy, to change. This is known to occur in Cu and Au where optical transitions from the d bands to states near the Fermi level occur at 2.14 and 2.38 eV, respectively.[3,4] For these metals, prior to arrival of the pump pulse, almost no optical transitions can occur at 1.98 eV, since nearly all the final states are filled by electrons. After the arrival of the pump, the electron temperature rises, causing the tails of the Fermi distribution to spread out in energy (Fermi-level smearing), opening states below the Fermi level for transitions. These states then absorb photons from the probe pulse, which sees a corresponding increase in absorption. Thus, changes in T_e will cause changes in R. A moment's reflection shows that any transition involving states near the Fermi level will be sensitive to T_e, so we are not restricted to the noble metals in this experiment. Care must be taken, however, in interpreting the experimentally observed relaxation traces. Changes in the metal's reflectivity can also arise from lattice-temperature changes. For example, band shifting arising from thermal strain will cause the reflectivity to change.[9] Thus, the reflectivity of the metal will change in response to both ΔT_e and ΔT_l as

$$\Delta R = a\Delta T_e + b\Delta T_l , \tag{4}$$

where a and b are constant coefficients describing how electron heating and lattice heating affect R. ΔR arising from changes in T_l will typically decay on a very slow time scale ($\gg 10$ ps) determined by the rate at which heat can diffuse away from the optically pumped region. In fitting the data, we make the (physically reasonable) assumption that any relaxation signal occurring on a fast (≤ 1 ps) time scale is due to electronic relaxation alone.

The experimental ΔR vs t curves are computer fitted to the solution of (3) using a least-squares method with only $\lambda_{\rm exp}\langle\omega^2\rangle$ as the fitting parameter. The boundary values needed to solve (3) are $T_e(0)$ and $T_e(\infty)$: $T_e(0)$ is determined from the pump-laser energy and published values of the linear coefficient of the specific heat γ, while $T_e(\infty)=T_l(\infty)$, which is found from published values of the total specific heat of the metal and the pump energy. We find that the value of $\lambda\langle\omega^2\rangle$ derived from the fit is not sensitively dependent on the boundary values used. Furthermore, as mentioned above, changes in electron and lattice temperature may both give rise to ΔR as in (4); the ratio a/b is determined by comparing the peak of $\Delta R(t)$ to the value of ΔR after the fast transient has decayed away, corresponding to $T_e(\infty)$. The data are then fitted using the procedure commonly employed in fitting pump-probe data:[7] The impulse response of $R(t)$ [the solution of (3) inserted into (4)] is convolved with the pump-pulse intensity autocorrelation function, yielding a theoretical ΔR vs t curve which may be fitted to the data.

The various metal samples were deposited on clean glass slides by e-beam evaporation. The base pressure for evaporation was $< 10^{-6}$ Torr to insure sample purity. As described below, certain samples (see Table I) had a thin overlayer of Cu deposited on top of the evaporated metal sample. This layer was deposited without breaking vacuum to avoid contaminating the metal/Cu interface. All samples used were optically thin (sample thickness less than optical skin depth at 1.98 eV) so that the pump-laser energy was distributed uniformly over the depth of the sample. It is very important that the sample be optically thin so that there is no transport of heat[10] or electrons[11] out of the optically pumped region during the time over which electron temperature relaxation takes place—effects which can mask the desired relaxation signal.[11] After preparation, T_c of the superconducting films was measured using either a SQUID magnetometer or via a resistivity measurement.

Not all metals display a fast relaxation signal. This is because only a few metals have an optical transition near 1.98 eV which involves the Fermi level. In order to study important materials which do not have such a transition (viz., Nb, V, and Pb), we deposited a very thin overlayer (≤ 40 Å) of Cu on top of these samples immediately after they were deposited.[12] The electron temperature in the Cu overlayer is exactly the same as that in the metal under study. This occurs because the heat flow in thin (≤ 500 Å) metal films occurs at the Fermi

TABLE I. Experimental values for the electron-phonon coupling $\lambda_{\rm exp}$ and other parameters: initial electronic temperature $T_e(0)$, experimental value of $\lambda_{\rm exp}\langle\omega^2\rangle$, literature values of $\langle\omega^2\rangle$, and $\lambda_{\rm exp}$. Error in $T_e(0)$ is 20%. For comparison, values of the electron-phonon coupling $\lambda_{\rm lit}$ from the literature are also shown (where available).

	$T_e(0)$ (K)[a]	$\lambda_{\rm exp}\langle\omega^2\rangle$ (meV^2)	$\langle\omega^2\rangle$ (meV^2)	$\lambda_{\rm exp}$	$\lambda_{\rm lit}$
Cu	590	29 ± 4	377[b]	0.08 ± 0.01	0.10[b]
Au	650	23 ± 4	178[c]	0.13 ± 0.02	0.15[c]
Cr	716	128 ± 15	987[d]	0.13 ± 0.02	···
W	1200	112 ± 15	425[e]	0.26 ± 0.04	0.26[e]
V	700	280 ± 20	352[f]	0.80 ± 0.06	0.82[f]
Nb	790	320 ± 30	275[g]	1.16 ± 0.11	1.04[g]
Ti	820	350 ± 30	601[g]	0.58 ± 0.05	0.54[g]
Pb	570	45 ± 5	31[i]	1.45 ± 0.16	1.55[i]
NbN	1070	640 ± 40	673[j]	0.95 ± 0.06	1.46[j]
V_3Ga	1110	370 ± 60	448[k]	0.83 ± 0.13	1.12[k]

[a] γ values from Ref. 15 were used to determine $T_e(0)$.
[b] Reference 16.
[c] Reference 17.
[d] Reference 18.
[e] Reference 19.
[f] Reference 20.
[g] Reference 21.
[h] Reference 22.
[i] Reference 23.
[j] Reference 24.
[k] Reference 25.

velocity v_F.[10] Thus, T_e will be the same over the entire sample thickness in a time given by $\approx L/v_F$, which is ≈ 30 fs for a 300-Å film. Since the relaxation rate of T_e in Cu is very long (approximately several ps), and the Cu layer is very thin compared to the underlying metal, the relaxation rate of the composite structure is determined solely by the underlying metal. The Cu overlayer acts then as a thermometer, since its reflectivity is sensitive to T_e in the underlying metal. Using this method, we are able to extend the femtosecond pump-probe technique to metals which ordinarily do not display a fast T_e response at 1.98 eV.

The observed ΔR versus time delay t signals for several representative metals are shown in Fig. 1. The computer-generated fit is shown for each sample as the solid line. As can be seen, the theoretical fits to the relaxation data are quite close to the observed decay traces for delay times after the pump pulse. However, a slight delay ($\sim$20 fs) occurs between the rising edges of the theoretical fit and the data. This may signal the occurrence of a nonthermal distribution of electrons for these very short times. However, electron-electron scattering equilibrates the electrons among themselves very quickly, so the electrons form a thermal distribution among themselves during the time the sample is being irradiated by the pulse.[2,4] Such an effect will not hamper the measurement of λ, since electron-phonon relaxation takes place on a time scale longer than the pulse width.

The derived values of $\lambda_{exp}\langle\omega^2\rangle$ are given in Table I. Values for $\langle\omega^2\rangle$ were culled from the literature, and were used to get λ_{exp}. These results are summarized in Table I, where we also show the results of other published experiments measuring the electron-phonon coupling, λ_{lit}.

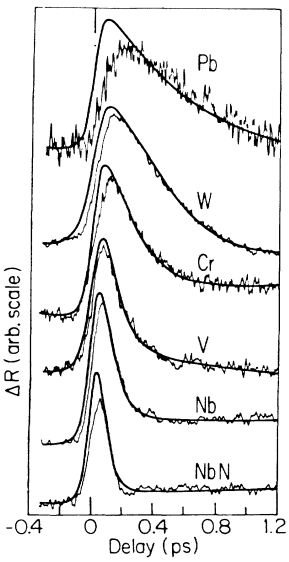

FIG. 1. ΔR vs t for Pb, W, Cr, V, Nb, and NbN. Numerical fits to the raw data are also shown.

In nearly every case the agreement is excellent, within experimental error. A little discrepancy occurs in the values obtained for NbN and V_3Ga. Inspection of Fig. 1 reveals that the response of NbN nearly follows the envelope of the pump pulse. This is because the relaxation time of T_e in NbN is on the order of the pulse width itself. This is similarly true of the V_3Ga data (not shown). Such behavior is consonant with Allen's theory: These materials have among the highest T_c's (for metals); thus, their relaxation times are the shortest. The values of $\lambda_{exp}\langle\omega^2\rangle$ and λ_{exp} for these samples given in Table I should cautiously be regarded as lower bounds.

We would like to highlight our value of λ_{exp} for Cr. To date, only a few—widely varying—values of λ for Cr have appeared in the literature.[13] It is well known that Cr is antiferromagnetic below 315 K; it is widely supposed that the antiferromagnetism contributes to the suppression of superconductivity. Estimates of λ based on resistivity data[13] do not account for the effect of the antiferromagnetism on the resistivity, and hence tend to overestimate λ.[14] Estimates of λ based on specific-heat measurements[13] tend to underestimate λ for the same reason.[14] Since our measurement of T_e relaxation is sensitive only to the electron-phonon interaction, the value of λ_{exp} given in Table I is probably the best determination of λ to date, and is certainly the first direct determination of this important quantity in Cr.

To insure that the Cu overlayer deposited on certain samples did not affect the experimentally observed relaxation process, we deposited Cu layers of different thicknesses on identical W samples. W has the property that a fast electronic relaxation signal can be observed even without a Cu overlayer. The overlayer thicknesses were 0 (no Cu), 40, and 100 Å. The 0- and 40-Å overlayer samples give similar values of $\lambda_{exp}\langle\omega^2\rangle$ (0-Å Cu, 112 meV^2; 40-Å Cu, 137 meV^2). The 100-Å overlayer sample gives a much lower value (65 meV^2) since the presence of the thicker Cu layer tends to decrease the measured relaxation time. From this, we conclude that thin (≤ 40 Å) Cu layers do not significantly perturb the relaxation process occurring in the underlayer.

On the V and Nb samples having a Cu overlayer, resistance measurements showed that T_c had dropped below 4 K in V and below 1.5 K in Nb. T_c measurements performed on samples made simultaneously with these, but having no Cu overlayer, showed the usual values of T_c. We attribute the suppression of T_c in the samples with overlayers to a proximity effect. This effect should not alter the values of $\lambda_{exp}\langle\omega^2\rangle$ we measure here, since $\lambda_{exp}\langle\omega^2\rangle$ depends on the phonon-mode spectrum and the electron-phonon matrix element, while the proximity effect is a purely electronic effect. This proximity effect did not occur in NbN samples prepared with Cu overlayers. (These samples are not shown in Table I.) This behavior is reasonable since the coherence length of both Nb and V is larger than the film thickness, while

the coherence length of NbN is smaller than the film thickness. Thus, the superconducting wave function in Nb and V is more seriously perturbed by the Cu overlayer than is the superconducting wave function of NbN.

In summary, we have performed the first femtosecond pump-probe measurements of λ in metals. This method has several advantages over other techniques (e.g., tunneling or heat-capacity measurements): it is a direct measurement of $\lambda\langle\omega^2\rangle$, it works at room temperature, it can be applied to both superconducting and nonsuperconducting samples, and it is not affected by extraneous effects such as the antiferromagnetism in Cr. By depositing thin Cu overlayers when necessary, our technique is extendable to nearly any metallic thin film. Finally, the agreement between our measured λ_{exp} values and those available in the literature is excellent, thus confirming the predictions of Allen.[1]

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