Hot-electron thermalization in solid and liquid argon, krypton, and xenon

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A delay in the development of conductivity following subnanosecond pulse irradiation of liquid and solid argon, krypton, and xenon has been found and is attributed to the relaxation of the initially superthermal electron energy distribution. The time scales required for thermalization are in agreement with values expected on the basis of interactions with acoustical phonons and with estimates derived from the field-strength dependences of the electron mobility.

The transport properties of excess electrons in the solid and liquid phases of the heavier rare gases argon, krypton, and xenon at close to their triple points[1] resemble closely the room-temperature properties of conduction electrons in the crystalline semiconductor materials silicon and germanium.[2,3] For all of these media, the low-field electron mobilities lie within the range of circa 500 to 5000 $cm^2\ V^{-1}\ s^{-1}$ and hot-electron effects become apparent as a monotonic decrease in mobility with increasing field strength. At high enough field strengths an almost field-strength-independent drift velocity of the electrons is observed. Significant differences appear only in the magnitude of the field strengths at which hot-electron effects become apparent (1 to 2 orders of magnitude lower for the rare-gas systems) and in the values of the high-field limiting drift velocities attained (appreciably higher for Si and Ge). These differences can be explained by a greater rate of electron energy dissipation in the semiconductor materials due to interactions of electrons with optical phonons.[4]

Since optical phonon modes are absent in the face-centered-cubic lattices of the rare gases, these media provide model systems in which to study effects due to acoustical phonons alone. In addition using the heavier rare gases, effects due to loss of long-range order on melting and further changes on reduction of the density of the fluid can be readily investigated without the need of excessive temperatures or pressures. Current interest in the practical consequences of both hot-electron effects and the transition from the crystalline to the amorphous state would suggest results on electron behavior in the rare-gas systems to be of particular interest at the present time. Several experimental studies of the mobilities of electrons in Ar, Kr, and Xe have been made to date.[1,5-9] In the present Communication we present data on the rate of energy degradation.

From a consideration of the field-strength dependence of the electron mobility in solid and liquid Ar, Kr, and Xe the times required for the thermalization of initially hot electrons in these media are expected to be on the order of nanoseconds.[10] Since ionization of a medium with photon or high-energy particle radiation invariably results in the formation of electrons with excess kinetic energy and since superthermal electrons have a reduced mobility, the relaxation of hot electrons should be observable as a delayed increase in the conductivity of the medium following pulsed ionization. The present work was initiated in an attempt to observe such effects using a pulse radiolysis microwave conductivity technique with subnanosecond time resolution.

The media were ionized using subnanosecond-duration pulses of 3-MeV electrons from a Van de Graaff accelerator. Total doses in the pulse were within the range 0.5 to 10 rad, giving charge carrier concentrations of less than 5×10^{13} particles cm^{-3}. The conductivity change was monitored using basically the same microwave absorption method as used previously to study electron thermalization in gases[11] and ionization in molecular liquids.[12] In the present case the 26–42-GHz frequency band was used. This allowed the use of small samples (circa 0.2 cm^3) and a cell construction which could be pressurized to 200 atm. The ac field strength (circa 10 V/cm) was sufficiently low that effects due to heating of electrons by the probing microwaves could be neglected. Transient changes in detector output were measured using a low-jitter pretrigger and sequential sampling system[13] with a rise time of 30 ps. Computer averaging was used to increase the signal-to-noise ratio. The gases were purified by passage over calcium and titanium at 600 °C. As a test of the absence of molecular impurities, the electron drift velocity was measured in the gas phase at high-field strength.[14]

The overall rise time of detection was determined by measuring the conductivity transient in liquid methane for which the electron thermalization time has been estimated to be on the order of 10 ps.[10] The methane data are shown in the insert to Fig. 1. The line drawn through the data was calculated using

a convolution program with a 10% to 90% Gaussian time response of 550 ps. The same rise time was found for the conductivity transient in a pulse-irradiated sample of crystalline silicon (30-Ω cm n type) which is also shown in the insert to Fig. 1. This rise time is considered to be due mainly to the response of the microwave detector (1N53D in a PRD 6606 FI mount).

In Fig. 1 are shown the conductivity transients observed in pure liquid and solid argon, krypton, and xenon at close to their triple-point temperatures. For all of these media a longer rise time of the conductivity transient was found than in the liquid methane and crystalline silicon samples. Shorter rise times were found in samples which were not subjected to rigorous purification.

As can be seen from the data in Fig. 1, the growth in the conductivity is followed at longer times by a decay. The rate of this decay was found to increase with increasing dose in the pulse and is attributed to electron–positive-ion recombination. By analysis of the data, taking into account this decay and the time response of detection, the contribution to the rise time of the transient due to the delayed development of the conductivity alone was derived. The values listed as measured thermalization times in Table I are the times required for 10% to 90% development of the conductivity, the assumption being made that this delayed development is due to the increase in electron mobility which is expected to accompany hot-electron thermalization. In support of this interpretation, the values found are of the same magnitude and show the same trends as rough estimates of thermalization times derived on the basis of simple energy balance arguments and the field-strength dependence of the mobilities using the relationship[10]

$$\tau_{\text{th}} \simeq \frac{3k_B T \ln[10(K_0/K_{\text{th}}-1)]}{20|n|e\mu_0 E_{10}^2} \quad . \tag{1}$$

In (1), k_B is the Boltzmann constant, T is the temperature of the medium, K_0 and K_{th} are the initial and thermal mean electron energies, n is the power dependence of the mobility on electron energy, e is the electronic charge, μ_0 is the low-field mobility, and E_{10} is the field strength at which the mobility deviates 10% from the low-field value. The estimated values of τ_{th} listed in Table I were obtained using the experimental data of Miller, Howe, and Spear[1] and taking $K_0 = 1$ eV and $n = -0.5$ as suggested by theoretical considerations discussed below.

For the condensed rare-gas systems, electron momentum and energy exchange with the medium are expected to be controlled by deformation potential scattering due to longitudinal acoustic waves.[4,15,16] Taking as a first approximation the energy distribution of superthermal electrons to be Maxwellian with a characteristic temperature T_e, then the mean rate of cooling of electrons can be represented by[4]

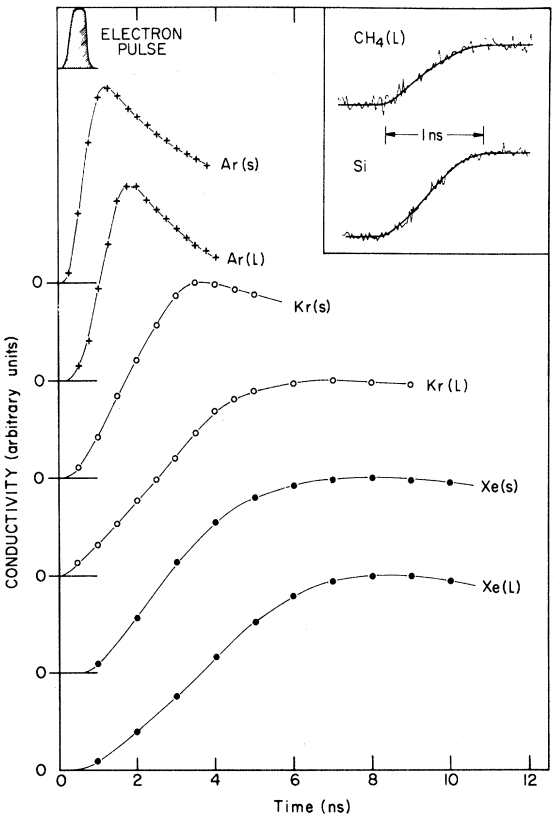

FIG. 1. The transient conductivity resulting from pulsed irradiation (0.4 ns) of liquid (l) and solid (s) rare gases at close to their triple-point temperatures. The transients have been normalized to the same height at maximum signal. Insert: Conductivity transients in liquid methane and crystalline silicon.

$$\frac{dT_e}{dt} = -A\left(\frac{T_e}{T}\right)^{1/2}(T_e - T) \tag{2}$$

with

$$A = \frac{16\sqrt{2}}{3\pi^{3/2}} \frac{E_1^2 m^{5/2}}{\hbar^4 \rho}(k_B T)^{1/2} \quad . \tag{3}$$

In (3), E_1 is the change in level of the bottom of the conduction band for unit dilation of the medium, m is the effective mass of the electron, and ρ is the density of the medium. The mobility, according to

TABLE I. A tabulation of measured hot-electron thermalization times and those calculated using Eqs. (1) and (8). Also listed are values of the longitudinal sound velocity, u_1, zero-field electron mobility, μ_0, and critical-field strength, E_{10}, for the solid (s) and liquid (l) media at temperature T.

Medium[a]	T (K)	u_1 (10^5 cm s^{-1})	μ_0 (cm^2 V^{-1} s^{-1})	E_{10} (V cm^{-1})	Thermalization time (ps) Eq. (1)[b]	Eq. (8)	Measured[c]
Ar (s)	82	1.38	1000	320	150	410	500 $\left[{+100 \atop -400}\right]$
Ar (l)	85	0.85	475	270	460	530	900 (±200)
Kr (s)	113	1.1	3700	70	1200	3300	2200 (±200)
Kr (l)	117	0.7	1800	60	3400	4100	4400 (±200)
Xe (s)	157	1.1	4500	55	2000	5500	4400 (±400)
Xe (l)	163	0.65	2200	45	6300	8100	6500 (±500)
Si (s)	298	9.2	1800	2000	6	59	· · ·
Ge (s)	298	5.4	3800	700	25	365	· · ·
CH_4 (l)	111	1.4	400	1500	22	220	· · ·

[a]The parameters listed were obtained for the rare gases from Ref. 1 (Table I and Fig. 9); for Si and Ge from Refs. 2 and 3 and from J. B. Gunn, J. Electron. 2, 87 (1956); A. F. Gibson and J. W. Granville, *ibid.* 2, 259 (1956); and M. B. Prince, Phys. Rev. 92, 681 (1953); and for CH_4 from Ref. 8 and from G. Bakale and W. F. Schmidt, Z. Naturforsch. 28a, 511 (1973).
[b]Taking $K_0=1$ eV and $n=-0.5$.
[c]Present work, in brackets are given error estimates.

deformation potential theory,[4] is given by

$$\mu=\frac{16\sqrt{2}}{3\sqrt{3\pi}}\frac{eu_1^2}{(k_BT)^{1/2}(k_BT_e)^{1/2}}\frac{1}{A} \tag{4}$$

$$=\mu_0(T/T_e)^{1/2}\ , \tag{5}$$

where u_1 is the longitudinal sound velocity.

On substituting for T_e as variable in (2) and integrating, with the initial condition $\mu/\mu_0 \ll 1$ at $t=0$ (i.e., $T_e \gg T$ at $t=0$), one obtains as a first approximation for the relaxation of the mobility of hot electrons

$$[(\mu_0/\mu)+1]/[(\mu_0/\mu)-1]=\exp(At)\ . \tag{6}$$

The thermalization time τ_{th}, defined here phenomenologically as the 10% to 90% rise time of the conductivity transient, is then

$$\tau_{th}=2.74/A \tag{7}$$

or, in terms of the measurable parameters μ_0 and u_1,

$$\tau_{th}=1.12(k_BT/e)(\mu_0/u_1^2)\ . \tag{8}$$

Energy relaxation data can therefore provide a quantitative test of deformation potential theory without requiring knowledge of the parameter E_1 or the relevant value of the electron mass. It should be pointed out here that deviations from the simple deformation potential theory, as represented by Eqs. (2)–(4), have in fact been found at high electric fields for the rare-gas systems.[1] Since the overall time taken for energy relaxation to within say 10% of thermal is controlled to a large extent by exchange processes occurring for energies not too far removed from thermal, the present data in the form of τ_{th} provide in fact a test of deformation potential theory only in the low-energy range. A more detailed analysis of the form of the conductivity transient should provide a more rigorous test of theory.

The values of τ_{th} derived from (8) for the present systems using measured values of the mobility of electrons and the velocity of sound are listed in column 7 of Table I. The agreement with the experimental values is seen to be quite good in particular for Kr and Xe. The higher rate of energy loss in the solid phase than in the liquid is seen to be predicted by the theory. This latter effect, which at first might be considered surprising in view of the decrease in collision frequency on solidification (as evidenced by the increase in mobility), is due to the much lower effective phonon mass, M^*,[4] in the solid.

$$M^*=\frac{3\sqrt{\pi}}{8}\frac{k_BT}{u_1^2}\ . \tag{9}$$

The resulting increase in fractional energy loss per collision, $2m/M^*$, more than compensates for the decrease in the collision rate.

The present results indicate the deformation potential approach to electron medium interactions to be equally well applicable to the liquid at close to the freezing point as to the solid despite the loss of long-range order. The increase in thermalization time on melting of the rare-gas solids has been found to continue as the density of the liquid is further reduced.[17]

The considerably shorter thermalization times estimated for silicon and germanium from experimental mobility data using (1) compared with that expected on the basis of Eq. (8) as shown in Table I have been attributed to energy loss by electrons to optical modes in these hexagonally arranged crystals.[4] Since for methane the packing is face centered cubic as for the rare gases studied, optical vibrational modes of the medium cannot be responsible for the excessive rate of energy loss. Apparently energy transfer to internal vibrational modes of the molecule play an important role in this case.

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