

# Electron dynamics of aluminum investigated by means of time-resolved photoemission

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## ABSTRACT

Femtosecond time-resolved two photon photoemission has been used to investigate the dynamics of photoexcited electrons at a polycrystalline Al surface. The measured relaxation time data are very different from the behavior predicted for a Fermi Liquid. We observed a distinct increase in the decay rate of the excited states. The origin of this strong deviation from the theoretical prediction may be transport effects or band structure effects induced by the periodic crystal lattice.

**Keywords:** electron-electron scattering, two pulse correlation, surface, time-resolved photoemission, aluminum

## 1. INTRODUCTION

For optical radiation in the visible wavelength regions, the photons are absorbed in solids by the creation of carriers, i.e. through the production of electron-hole pairs. Initially these carriers are far from being in equilibrium with the temperature of the substrate or even with the electron gas itself. A finite time is required for the 'nascent' electrons to reach equilibrium with each other to establish a temporally increased Fermi-Dirac distribution. Here we are interested in the detailed dynamics of the first steps in the relaxation of the nascent distribution to Fermi-Dirac, that is the relaxation of single excited electronic state.

The lifetime of a single electronic excitation is controlled by the available decay channels, which generally include collisions with other electrons, holes, phonons, plasmons, defects, and impurities. The ultrafast dynamics of optically excited carriers are being studied quite intensively for semiconductors, especially GaAs. Time domain studies have provided valuable information on the role of the various interaction mechanisms for the thermalization and relaxation process<sup>1</sup>.

In the case of metals of which the unoccupied orbitals are not restricted by a band gap, the hot electrons relax directly to thermal equilibrium with the whole electron gas. Therefore, the lifetime of individual excited electronic states is always short, typically in the order of only a few femtoseconds and, hence, a detailed study of relaxation phenomena in the time domain has just begun<sup>2-5</sup>. In metals the important decay channels at low carrier density are quite different compared to semiconductors. Carrier-phonon interaction and carrier-photogeneration processes play minor roles in the energy relaxation of hot electrons. Only at energy close to the Fermi level, where the inelastic lifetime increases rapidly, does electron-phonon scattering become more important. At low excited carrier density, the dominant hot electron relaxation process is inelastic scattering of the excited electrons with electrons of occupied states at and below the Fermi level, leaving both electrons in unoccupied states above the Fermi level. Defects, impurities and, for polycrystalline samples, grain boundaries will increase the elastic scattering rate but have a negligible effect on the inelastic scattering rate.

In contrast to hot-carriers studies in semiconductors, there are only few theoretical studies on metals, because the electron-electron scattering process in a metal is determined by the complicated competition between the available phase space for the transitions and the screening effects by the electron plasma. Unfortunately, no mathematically rigorous methods of treating many-body effects exist for most real metals. One must rely on different intuitive approximations and hope that they contain the important physics of the properties being investigated<sup>6</sup>. Most theoretical approaches are based on the Landau theory of Fermi liquids, which treats the excitation as a quasiparticle<sup>7</sup>. This theory is strictly valid for a Fermi liquid-like free electron gas only. However, as has been shown by Quinn, the relaxation process of a degenerate nearly free electron gas of some metallic conducting band may still be in a reasonable quantitative agreement with the FL-theory within certain limits<sup>8</sup>.

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Therefore, the first measurements have as their aim the comparison of experimentally determined lifetime values with the Fermi-Liquid theory. The mono-valent noble metals seem to meet most of the requirements for a degenerate, free electron gas. The obtained experimental results for noble metals were, however, quite controversial and initiated a debate as to whether the FL approach or the used technique, TR-2PPE, is responsible for the deviation between experiment and theory. There is, however, a metal, aluminum, which can meet the required conditions for a nearly free electron gas even better than the noble metals.

In this paper we will discuss the application of TR-2PPE, based on the equal pulse correlation technique, for studying the lifetime of electronic excitation in aluminum. In the next section, we will first review the theoretical results concerning the dynamical properties of low energy excitations of a Fermi Liquid. A short overview of the used technique, TR-2PPE, will be given in the following. Finally, results of experiments on polycrystalline aluminum will be analyzed and discussed in some detail.

## 2. DYNAMICS OF LOW ENERGY EXCITATIONS OF A FERMI LIQUID

The lifetime  $\tau_{ee}$  of a single particle excitation of an electron gas, as determined by electron-electron interaction, can, in principle, be calculated from the imaginary part  $E_I$  of its self energy  $E(p)$ . Quinn and Ferrell treated this problem in a theoretical study considering a Fermi liquid-like free electron gas<sup>9</sup>. In the case of low excitation energies  $E(p)$  and when the effect of plasmon creation can be excluded ( $E(p) \ll \hbar\omega_p$ ), they derived the following formula for  $E_I$ :

$$E_I(p) = -\frac{e^2}{2\pi^2} \frac{E^{(p)}}{E_F} \int \frac{d^3q}{q^2} \frac{\varepsilon_2(q, \Delta E(q))}{|\varepsilon(q, \Delta E(q))|^2}, \quad (1)$$

where  $\varepsilon = \varepsilon_1 + i\varepsilon_2$  is the complex dielectric function of the electron gas and  $\Delta E(q)$  is the energy transfer through the interaction of the excited electron with the electron gas at momentum exchange  $q$ . The decay time of the excitation is then given by

$$\tau_{ee} = \frac{1}{2|E_I(p)|} \quad (2).$$

The integrand in equation (1),  $\frac{\varepsilon_2}{|\varepsilon|^2} = \text{Im}\left(-\frac{1}{\varepsilon}\right)$ , is referred to as the energy loss function of an electron inside a bulk. This expression can be derived ‘easily’ by considering the power loss of a charged particle due to the dielectric shift inside a bulk<sup>10</sup>. Consequently,  $E_I(p)$  results from the sum of all possible decay channels of an electron, provided by the interaction with the electron gas. In detail,  $\varepsilon_2$  serves as a measure of the number of states available for real transitions due to interaction with the electron gas, whereas the denominator  $|\varepsilon|^2$  accounts for the screening of these interactions by the electron plasma<sup>8</sup>. It is the competition between transitions and screening which ultimately determines the lifetime of an excitation.

Quinn suggested that the screening of electron-electron interactions is sufficiently considered by the Thomas-Fermi dielectric function  $\varepsilon^{TF}(q, \Delta E(q)=0)$  if the energy of the excited electron  $E(p)$  is close enough to the Fermi energy  $E_F$ <sup>8</sup>. In this case, the denominator of the equation (1) can be replaced by

$$\varepsilon(q, \Delta E(q)) \cong \varepsilon^{TF}(q, 0) = 1 + \frac{q_s^2}{q^2};$$

$$q_s^2 = 4 \cdot (3/\pi)^{1/3} \cdot \frac{n^{1/3}}{a_0} \quad (3),$$

where  $q_s$  is the inverse Thomas-Fermi screening length,  $n$  the density of the electron gas and  $a_0$  the Bohr-radius. With respect to screening this approach considers that the system is always in equilibrium. The electron gas reacts instantaneously to changes induced by interaction with the excited electron and screens such disturbances within a typical length of  $1/q_s$ .

Under these conditions, Quinn derived the following simple expression of the lifetime  $\tau_{ee}$  in a 3D system which is known as Fermi-liquid behavior:

$$\tau_{ee} = \tau_0 \cdot \frac{E_F^2}{(E - E_F)^2}. \quad (4)$$

The prefactor  $\tau_0$  is approximately given by<sup>11</sup>

$$\tau_0 \approx \frac{64}{\sqrt{3} \cdot \pi^{5/2}} \cdot \frac{\sqrt{m}}{e} \cdot \frac{1}{\sqrt{n}}.$$

If we take into account that the Fermi energy  $E_F$  is also a function of the electron density  $n$ , then the dependence of  $\tau_{ee}$  can be given as

$$\tau_{ee} = \text{const} \cdot \frac{n^{5/6}}{\delta E^2}. \quad (5)$$

According to these assumptions, the inelastic lifetime of an excited electron, as a function of its excitation energy  $\delta E$  with respect to the Fermi edge  $E_F$ , is determined by the density  $n$  of the electron gas.

To account for the possibility of plasmon creation, Quinn restricted the validity of this equation to a range of  $E(p) < 1.7E_F$ . He also mentioned that his ‘dielectric constant’ approach to the electron-electron interaction, resulting in equation (1), is valid only for electron densities corresponding to  $r_s/a_0 < 1$ . However, it may be applicable even in the range of  $r_s/a_0 < 2$ .

	<b>Aluminum</b>	<b>Copper</b>	<b>Silver</b>	<b>Gold</b>
<b><math>r_s/a_0</math></b>	2.07	2.67	3.02	3.01
<b><math>E_F</math> [eV]</b>	11.7	7.00	5.49	5.53
<b>d-band onset [eV]</b>	-	2	4	2
<b>Valence</b>	3	1	1	1
<b><math>\tau_0</math> [fs]</b>	0.35	0.5	0.6	0.6

Table 1: Characteristic free electron properties of the selected metal samples.  $r_s/a_0$  is the radius of the free electron sphere,  $E_F$  the calculated Fermi energy, valence the number of conducting electrons per atom,  $\tau_D$  the Drude relaxation time and  $\tau_0$  the prefactor in equation (4). In addition, the onset of the d-bands below the Fermi edge is given. (Data taken from reference 7).  $\delta \epsilon_1(\omega \rightarrow 0)$  is the measured deviation from a Drude dielectric function (reference 15).

## Conducting electrons of metals as ‘real’ Fermi liquid

The conducting band of metals represents a degenerate, *nearly* free electron gas. This would enable the approximation of the dynamical behavior of electronic excitations of a conducting band due to electron-electron scattering by equation (4). However, one must consider that what actually happens is different from the ideal system assumed by Quinn. Ritchie and Ashley, for example, found that exchange processes, which arise because of the anti-symmetry of the wave function of the free electron gas can affect the lifetime of electronic excitation<sup>12</sup>. For high electron densities ( $r_s/a_0 \rightarrow 0$ ), the authors found only a slight effect of exchange processes on the lifetime  $\tau_{ee}$ . However, it might become more important under the conditions in real metals. In addition, Adler estimated the effect of non-sphericity of the Fermi surface<sup>13</sup>. He finds that, due to deviation from the spheric Fermi-surface, the rate of energy loss may be appreciably larger than expected from the Fermi liquid approach. A further correction of equation (4), corresponding to the influence of d-bands, has been made by Quinn<sup>14</sup>. Therefore, we may observe only a more or less quantitative agreement of our data as predicted by the Fermi liquid theory. To avoid overly large deviations, as discussed above, we should consider the following points when selecting metals for our study:

- 1) The conducting band should show a high valence electron density  $n$  (small value of  $r_s/a_0$ ).
- 2) Compared to a free electron gas, the Fermi surface of the metal should be as undisturbed as possible (as spheric as possible).
- 3) The influence of d-bands (or higher momentum bands) on the properties of the conducting band should be negligible.

To examine the electron dynamics of a simple degenerate electron gas, we selected the conducting band of aluminum as a model system. As can be seen from characteristic data given in Table 1, the polyvalent aluminum seems to be a suitable example compared, for example, with the noble metals which have already been investigated by several groups<sup>4, 5, 16, 18</sup>. The electron density is nearly within the limit given for the approximate validity of equation (4). In addition, the (resulting) high value of its Fermi energy enables the investigation of excitation energies up to 7eV above the Fermi edge within the limitation of low energy excitations ( $E(p) < 1.7E_F$ ). This model-like character becomes more

reasonable due to the clear  $\sqrt{E}$  dependence of the calculated electronic state density of Al which matches the behavior of a three-dimensional free electron gas<sup>19</sup>. In addition, characteristic quantities, as calculated from the electron density according to the Drude theory, agree very well with the experimentally observed values. Electron loss experiments indicate a plasma frequency  $\hbar\omega_p = 15.0\text{eV}$  compared to the calculated  $15.8\text{eV}$ <sup>20</sup>. The Fermi energy  $E_F$ , as determined by X-ray photoemission, is in quite good agreement with the theoretical value of  $11.6\text{eV}$ <sup>21</sup>. The aluminum’s Fermi surface is also very close to the free electron surface for a face-centered cubic mono-atomic Bravais lattice with three conducting electrons per atom (trivalent metal)<sup>7</sup>. Moreover, in contrast to the noble metals, the free electron character of the valence band of aluminum is not disturbed by the presence of localized d-bands. Therefore, it is not surprising that, in many theoretical papers which treat the problems of a degenerate electron gas, results are given as calculated for  $r_s/a_0 \cong 2$  corresponding to the electron density of aluminum.

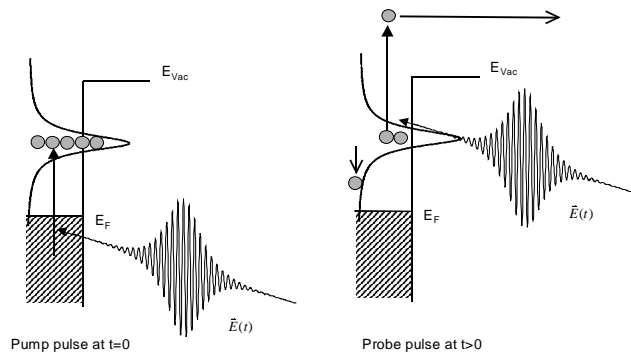


Figure 1: Principle of a pump and probe experiment combined with 2PPE. A first photon pulse, defining time zero of the experiment, excites electrons into an intermediate state; the remaining population of this state at  $t > 0$  is probed by the excitation of electrons into the vacuum by a second pulse. By a defined variation of the time delay between the pump and probe pulse, the depletion of this state in the time domain is successively measured.

### 3. TR-2PPE APPLIED TO THE INVESTIGATION OF VALENCE BAND EXCITATIONS IN METALS

The experimental method used to investigate the lifetime of electronic excitations of the metal conducting band is time resolved two photon photoemission (TR-2PPE). It enables a direct measurement of the dynamical properties in the time domain with a resolution of a few femtoseconds. The principle is systematically shown in Figure 1. A pump photon pulse induces the excitation of a single electron out of the valence band of the metal. A second probe photon pulse measures the population of the intermediate excitation, induced by the pump pulse, as a function of the temporal delay with respect to the pump pulse. In first order, the measured pump probe signal contains an exponential decaying contribution which is, in certain cases, directly correlated to the lifetime of the intermediate excitation.

#### Secondary electrons and transport effect

TR-2PPE probes the population decay of excited electrons in a defined energy range, given by the energy resolution of the electron analyzer. In the simplest case the decay of the probed intermediate state can be described by a rate equation model:

$$\frac{d}{dt}n_2 = A(t) \cdot n_1 - \frac{1}{\tau_{ee}}n_2. \quad (6)$$

Here  $n_1$  and  $n_2$  are the initial and intermediate population respectively, and  $A(t)$  is the transition probability per time unit between the two states induced by the interaction of exciting laser pulses and the dipole moment of the transition. A more correct description of the excitation process within a TR-2PPE experiment would require a quantum mechanical approach within the density matrix formalism. Under the experimental conditions, that is when the dephasing time of the excitation process is much shorter than the length of the exciting laser pulse, a description of this process within a rate equation model seems to be reasonable, at least in the case of bulk electron excitations in metals<sup>18, 22</sup>. The investigated systems and the experimental mode are, however, complex, and we have to carefully consider which additional processes next to the decay process might contribute to our measured signal. On the one hand, this mixing of different processes might be considered as a disturbance, on the other we should be aware that any further contribution to our signal contains additional information about the investigated system. The two processes described below might give rise to additional contributions to our TR-2PPE signal and will be discussed in some detail: the creation of secondary electrons following the primary excitation process induced by the laser and the transport of the electrons away from the probed surface region into the bulk.

#### Secondary processes

In addition to photo-excitation of electrons into the probed intermediate state, its population may be further increased by secondary processes, arising as a consequence of the primary excitation process (Figure 2). This is caused by

- 1) the inelastic decay of excited electrons from energetically higher lying states (cascade process),
- 2) electrons excited from the Fermi sea after interaction with already excited electrons (cascade process), and
- 3) relaxation of excited holes, created during the primary excitation process by means of Auger decay.

According to Quinn, the electron loses about 2/3 of its excitation energy during a typical collision<sup>8</sup>. Ritchie mentioned that this value decreases to one half if one takes the anti-symmetry

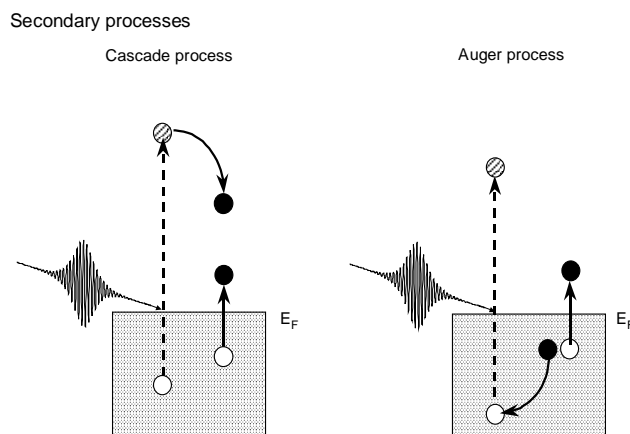


Figure 2: Secondary processes, left, cascade processes: population of states due to decay of electrons from higher states and electrons excited from the Fermi-sea due to scattering processes with primary electrons; right: population due to Auger-like decay processes of holes created during to the primary excitation step.

of the electrons wave function into account<sup>12</sup>. At a typical photon (excitation) energy of  $h\nu=3.3\text{eV}$ , the highest excited state probed in an experiment will be  $3.3\text{eV}$  above the Fermi level. Therefore, by a careful estimation, refilling processes due to these cascade processes in an energy range between about  $2\text{eV}$  and  $3.3\text{eV}$  should have only a minor effect on our experiment. In addition, for the investigated systems, equation (4) suggests relaxation times in the range of only a few fs at the high energy end, about  $3\text{eV}$  in our experiment. Considering the strong lifetime dependence given by the denominator  $(E-E_f)^2$ , this refilling of states should be instantaneous with respect to the intrinsic lifetime of the respective state, even at about  $2\text{eV}$ , and should not disturb our results to a great extent. For lower excitation energies, however, the effect on the refilling of an energetic population by cascades increases and might become substantial. In addition, the closer we get to the Fermi level, the greater the number of electron cascades of higher order built up by the first generation of cascade electrons. The decay of one single electron excitation results typically in the creation of two (low energetic) electron excitations. It is obvious that, in this energy range, it may occur that we measure a relaxation process determined by such cascades but no longer by the lifetime of a single excited electron<sup>18</sup>.

A further source of secondary electrons is the relaxation of holes, created by the primary photo-excitation step by means of Auger decay (Figure 2, right). If the dynamical properties of the electronic system can be considered to be symmetric to the Fermi edge with respect to exchange between the electron and the hole, then such a process should affect the measured signal in the same order as the electron-induced secondary electrons. Again, we expect a slight effect on high energy excitations with an increasing disturbance of excitations close to the Fermi edge.

One approach for including these secondary processes in a theoretical description of the 2PPE process would be to expand, for example, the rate-equation model corresponding to the intermediate state to

$$\frac{d}{dt}n_2(t) = A(t) \cdot n_1(t) - \frac{1}{\tau_{ee}}n_2(t) + C(E,t) + D(E,t), \quad (7)$$

where  $C(E,t)$  accounts for refilling due to the cascade electrons and  $D(E,t)$  for refilling due to electrons created by Auger decay of holes. Unfortunately, primary excitation and secondary processes with respect to the time axis are hardly distinguishable in an experiment. The strong deviation of measured cross-correlation traces from model simulations, as observed by Hertel *et al.* at a copper surface in a bichromatic TR-2PPE experiment<sup>3</sup>, might indicate such secondary processes. Simulations of cross-correlation traces, taking these secondary processes into account, have confirmed this interpretation<sup>18</sup>. Interestingly, the experimental data suggest that the deviations caused by these refilling processes become important at about half the maximum excitation energy and increase further as the Fermi edge is approached.

### Transport effect

The second factor which must be taken into account is the transport of the photoexcited electrons away from the probed surface region. In our experiment, this will reduce the photoelectron intensity emitted by the probe pulse out of the surface region and will set a lower limit for measured lifetimes by 2PPE. For example, even if the electrons had an infinitely long lifetime, there should still be an experimentally measurable decrease in the photoelectron yield as a function of pump-probe delay time due to the electron moving away from the surface and out of the probe volume. Using a simple approach, we might assume that a separate mechanism is responsible for decay and transport and, therefore, sum the measured decay rates in correspondence with Matthiessen's rule

$$\frac{1}{T_{meas.}} = \frac{1}{\tau_{ee}} + \frac{1}{T_{trans.}}, \quad (8)$$

leading in any case to  $T_{meas.} < \tau_{ee}$ . Hence, the depletion of an excited state population in the probed region, as a function of the time delay between the two pulses, depends on the intrinsic decay of the excited energetic state *and* on transport.

Model calculations of the transport effect on copper have been made by Schmuttenmaer *et al.*<sup>2</sup> using a ballistic model and by Knoesel<sup>23</sup>, who took the explicit band structure of different copper surfaces into account. As expected from equation (8), the transport may actually induce a strong deviation (reduction) of the measured lifetime compared to the intrinsic inelastic lifetime, depending on the ratio between  $T_{trans.}$  and  $\tau_{ee}$ . The calculation made by Schmuttenmaer *et al.* suggests a value of 30fs for  $T_{trans.}$ . Based on this model, which assumes the electron transport inside the bulk to be ballistic,

this value can be taken as the lower limit for  $T_{\text{trans}}$ . Any scattering process causes the electron to become confined to a certain degree within the surface region. Therefore, it should increase the effective transport time. The more realistic calculation of Knoesel gives values in the range of 50fs (depending on the pulse width of the exciting laser). In addition, he could show that equation (8) actually reproduces the lifetimes deduced from simulated correlation traces quite well, at least for lifetimes  $T_{\text{intr}}$  below 80fs. Very recent investigations of noble metal films evaporated on insulator substrates actually indicate the experimental importance of this transport effect<sup>25</sup>.

#### 4. EXPERIMENTAL SET-UP

The experimental set-up is described in more detail elsewhere<sup>4</sup>. In brief, our time-resolved two-photon photoemission experiments were performed with an 82 MHz pulsed Ti:Sapphire laser, tunable from 730 to 830 nm. The system delivers transform-limited and  $\text{sech}^2$  temporally shaped pulses of up to 9 nJ/pulse with a duration of 40 fs. The linearly polarized output is frequency doubled in a 0.2 mm thick Beta Barium Borate (BBO) crystal to produce UV pulses at  $h\nu = 3$  to 3.4 eV. The pulses are split by a beam splitter to equal intensity (pump and probe pulses), and one path is delayed with respect to the other by a computer-controlled delay stage. Both beams are combined colinearly by a second beam splitter and are focused under  $45^\circ$  incidence at the sample surface. For our studies of the relaxation dynamics of excited bulk electrons, only polycrystalline aluminum, cut from high purity commercial metal sheets, was used. The sample is mounted in an UHV-chamber (base pressure  $8 \cdot 10^{-11}$  mbar) equipped with a cylindrical sector analyzer. In general, we use a pass energy of 4eV, leading to roughly 50meV resolution. A 4.0V bias is applied to the sample to eliminate the effects of any stray electric fields. The sample was prepared by several sputtering and heating cycles. Sample cleanliness was checked by work function measurements, as determined by the onset of the 2PPE spectra and Auger spectroscopy and compared with the respective literature data. For some measurements cesium was deposited onto the aluminum surface by evaporation from a commercial SAES getter source to lower the work function. This enabled us to extend the accessible energy range to excitation energies down to 0.5 eV. The pressure during evaporation was maintained in the low  $10^{-10}$ mbar range. The effect of Cs on electron scattering is negligible: within the present time-resolution, in the case of a cross-polarized experiment, we did not observe a difference in the lifetime measurements on a clean Al surface and a Cs/Al surface at least in the overlapping energy region.

#### 5. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 shows the lifetimes determined from the correlation traces of the TR-2PPE measurements as a function of the electrons' excitation energy  $\delta\mathcal{E} = E - E_F$  for aluminum. The solid line represents the theoretical calculation for aluminum based on equation (4) and the pre-factor  $\tau_0$  as given in Table 1. The disagreement between theoretical and measured lifetimes in the case of aluminum is quite significant. The data do not fall within the range of the predicted lifetime and cannot be explained by the  $(E - E_F)^{-2}$  law. If we assume that we are probing the intrinsic, inelastic lifetime only in our experiment, then this result is surprising. Investigations of the noble metal silver showed a remarkable good agreement with Fermi-liquid behavior, although these

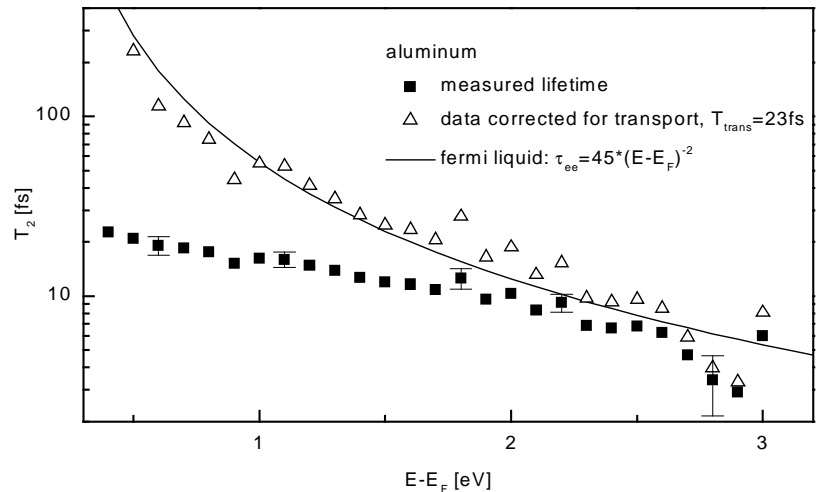


Figure 3: Lifetime data, as obtained for polycrystalline aluminum; the measured lifetimes are much shorter than expected from theoretical considerations, but can, however, be brought into line with Fermi liquid theory by including a (energy independent) transport time  $T_{\text{trans}}=23\text{fs}$ .

system is less suited for use of model system as stated above<sup>18, 22</sup>.

The qualitative results, deduced from the above discussion of secondary and transport effects, imply a correlation between this lifetime deviation and the ‘lifetime reducing’ transport term in equation (8). To estimate the lower limit of  $T_{\text{trans}}$  of aluminum we scaled the transport time value  $T_{\text{trans}}$  of copper ( $\approx 30\text{fs}$ ), as calculated by Schmuttenmaer for the ballistic transport, by the ratio of the Fermi velocity of copper to that of aluminum:

$$T_{\text{trans}}^{\text{Al}} \approx T_{\text{trans}}^{\text{Cu}} \cdot \frac{v_F^{\text{Cu}}}{v_F^{\text{Al}}} = T_{\text{trans}}^{\text{Cu}} \cdot \frac{\sqrt{E_F^{\text{Cu}}}}{\sqrt{E_F^{\text{Al}}}}$$

Taking  $E_F^{\text{Cu}} = 7\text{eV}$  and  $E_F^{\text{Al}} = 11.6\text{eV}$ , we obtain the value of  $T_{\text{trans}} \approx 23\text{fs}$ . From equation (8) we can recalculate  $T_{\text{decay}}$ . The result is shown in Figure 3 ( $\Delta$ ). The agreement with Fermi liquid theory is now nearly perfect. However, despite the excellent agreement between scaled experimental data and theory, the result is surprising, because such a *significant* transport contribution to the measured lifetime could not be proved using any other investigated system, namely the noble metals. It is also questionable as to whether a ballistic model of transport and, thus, these short transport times are reasonable, at least at room temperature. Conductivity measurements show a very effective scattering rate (‘momentum loss rate’), especially in the case of aluminum. At 273K the average electron-phonon scattering time of aluminum can be estimated to be 8fs compared to 29fs for copper<sup>7</sup>. Thus, the aluminum electron has scattered three times during the course of ‘ballistic’ transport. This behavior suggests a certain degree of confinement of the electrons within the investigated surface region, whereby, in contrast to a ballistic assumption, the transport time would be more likely to be longer than for copper. Unfortunately, a more realistic calculation of the transport effect for this system has not yet been made. Even the transport calculations made by Knoesel for copper (based on its detailed band structure) show qualitative trends but could not give a satisfactory quantitative description of the experimental results<sup>23</sup>.

Because of this uncertainty regarding the transport term it is advisable to find another mechanism, which might be responsible for the observed strong deviation of the behavior of aluminum from a Fermi liquid. This may be possible if we take a closer look at the detailed band structure of this metal.

As stated above, the dielectric function determines the rate of energy loss of an electron due to its interaction with the electron gas. Optical absorption and reflectivity measurements of solid aluminum show a deviation of  $\epsilon_2(0, \omega)$

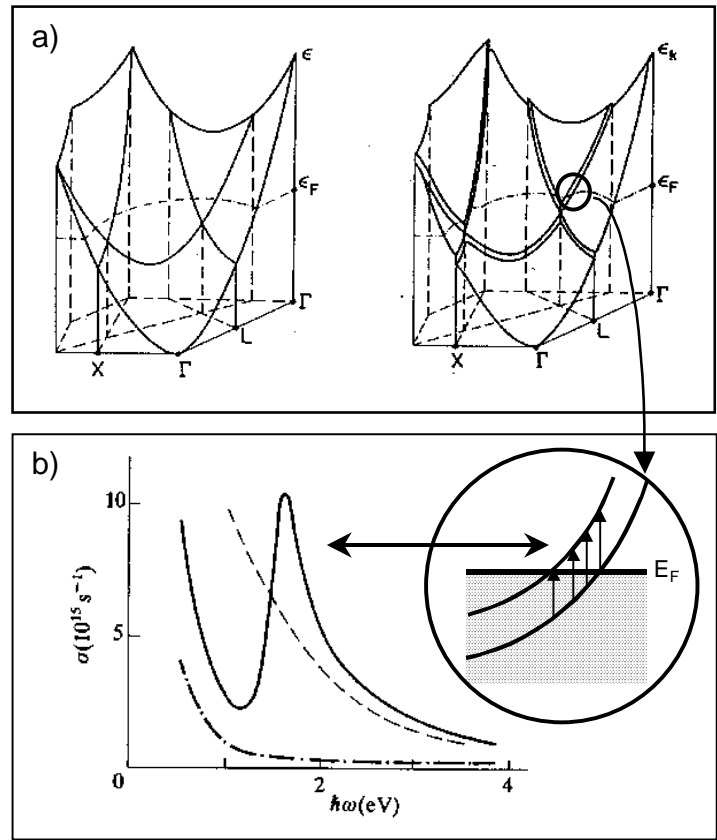


Figure 4: a) Splitting of the degenerate band induced by the periodic lattice potential; left: empty lattice free-electron bands in Al appropriate to a section in a (110) plane; right: splitting and appearance of parallel bands due to a small, effective crystal potential. The parallel bands offer a new kind of excitation channel for optical transition and, vice versa, new decay channels to an excited electron (26) b) Unbroken line: optical conductivity  $\sigma(\omega) = \omega \cdot \epsilon_2(\omega)$  for an evaporated Al film. In addition,  $\sigma(\omega)$  for a Drude-like metal (---) and liquid aluminum at 900K (—) is shown (28). The pronounced peak at  $\hbar\omega \approx 1.5\text{eV}$  for solid aluminum is due to an interband transition as described in the text.



from the behavior of the free electron gas in the low energy excitation regime, indicated by a pronounced absorption peak at  $\hbar\omega \approx 1.5\text{eV}$  (Figure 4b). As shown by Ashcroft and Sturm<sup>26</sup>, this structure must be attributed to the interaction of the electron gas of a polyvalent metal with a (periodic) lattice potential. The latter breaks up the degeneracy of the different valence bands in certain directions in  $\vec{k}$ -space, resulting, as in the case of the trivalent aluminum, in a parallel band spectrum (Figure 4a). The high number of electrons of the trivalent aluminum allows a (partial) occupation of these bands. Absorption of photons occur at points in  $\vec{k}$ -space where the Fermi edge crosses these parallel bands and direct excitation of electrons from the lower (occupied) band to the higher (unoccupied) becomes possible. The pronounced absorption peak can be attributed to an interband transition of the absorbing electron between such parallel bands located at directions which are parallel to the (100) face. A further, similar band transition at energies of  $\Delta E=0.5\text{eV}$  has been predicted theoretically and has also been observed for directions parallel to the (111) face<sup>27</sup>.

What does this mean for the investigated electron-electron scattering process? Such interband transitions may have drastic consequences for the allowed energy transfers, that is for the available phase space for inelastic of the dielectric constant, are determined by the parabolic energy dispersion of the electron gas  $E(\vec{k}) = \hbar k^2 / 2m_e$ . In the case of photon-absorption in aluminum, a phase-space increase in absorption arises from the additional excitation channels, offered by the parallel band structure to the absorbing electron (e.g. at  $\Delta E=1.5\text{eV}$  and  $\vec{k}=0$ ). For electron-electron interaction, the phase-space increases further, because here *both* scattering partners can make use of the increased phase space: the parallel bands are not exclusively located at the Fermi edge but extend over a rather large energy range above  $E_F$ . The multitude of possible transitions may increase significantly. In terms of the imaginary part of the dielectric function  $\varepsilon_2(q, \Delta E)$  and its effect on the inelastic lifetime, a quantitative estimation cannot be given within the scope of this paper. Qualitatively, we expect an increased scattering rate induced by the additional decay channels in agreement with our observation. In undertaking a quantitative analysis, it might be necessary to consider the screening effects induced by a  $\Delta E \neq 0$  component of  $\varepsilon(q, \Delta E)$  of the electron gas due to these interband transitions, beyond the adiabatic screening approach assumed by Quinn.

The result obtained with the ‘simple’ Fermi liquid-like metal aluminum indicates that it is not so easy to interpret the data of TR-2PPE measurements in terms of a quantitative analysis which compares experiment and theory. More detailed experiments are required. In the present case, we have to find a way of distinguishing between two possible effects, transport and parallel band decay. One way of gaining insight into the former mechanism would be to investigate aluminum films evaporated on an insulating substrate on films of varying thickness. The insulator at the back of a sample would hinder the electrons from drifting away into the bulk. Low temperature measurements might also help us to understand the influence of transport (change in electron-phonon scattering rate).

Parallel band formation could be avoided by using amorphous or liquid samples. Crystal structure effects cannot influence the electron dynamics any further. Therefore, in the case of liquid aluminum, the pronounced 1.5eV photon absorption peak was reported to disappear<sup>29</sup> (Figure 4b). An investigation under surface science conditions (UHV) can be realized by local surface melting with a high-powered laser pulse just before a pump-probe scan. An advantage of such an experiment would be that it is possible to compare directly the different behavior of the bulk and liquid using the same sample.

## 6. SUMMARY

Despite the nearly model-like properties of the conducting electrons of aluminum with respect to a Fermi liquid, we showed that the corresponding dynamics of electronic excitations, as measured by TR-2PPE, deviate strongly from the predictions. However, we were unable to determine whether this behavior is the result of the experimental approach (transport effect) or of an intrinsic property of the sample (e.g. a band structure effect induced by the periodic crystal lattice).

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