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MEMORANDUM

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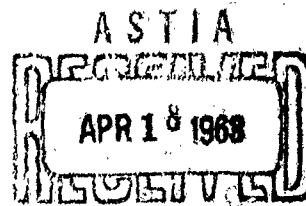
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THE INTERACTION OF
LASER LIGHT WITH METALS
(Electron-optical phonon interaction in metals)

H. T. Yura

PREPARED FOR:

UNITED STATES AIR FORCE PROJECT RAND



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The RAND Corporation
SANTA MONICA • CALIFORNIA

MEMORANDUM

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MARCH 1963

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PREFACE

As part of their continuing program, RAND's Physical and Quantum Electronics Group selects theoretical topics for study which should be of ultimate interest to the Air Force. The present study gives a calculation of the time required for metals to vaporize when subjected to a laser beam. The theoretical study presented here should serve as a guide to future experimental work.

SUMMARY

In this Memorandum we consider the interaction of laser light with a metal. A model is proposed in which the dominant mechanism for electron de-excitation in transition metals is by the emission of optical phonons, as contrasted to the simple metals where the dominant mechanism is by the emission of acoustic phonons. Calculations based on this model give, for steel, an electron--optical phonon relaxation time $\sim 10^{-7}$ to 10^{-6} sec compared with an electron--acoustic phonon relaxation time $\sim 10^{-11}$ to 10^{-10} sec for a simple metal such as copper.

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LIST OF SYMBOLS

D	density of final states
E_F	Fermi energy
I	integral defined in Eq. (20b)
$\bar{L}$	general lattice vector
M	matrix element of the electron--optical phonon interaction
$M_{1,2}$	masses of the atoms in the unit cell
m	effective mass of s-band electrons
N	number of unit cells per cc
n	number of conduction electrons per cc
P_F	Fermi momentum
R	Rydberg
Γ_1	first-order electron--optical phonon transition probability
Γ_2	second-order electron--optical phonon transition probability
τ_1	first-order electron--optical phonon decay time
τ_2	second-order electron--optical phonon decay time
ω_0	optical-phonon frequency

I. INTRODUCTION

In this Memorandum we investigate a mechanism by which excited conduction electrons in a metal may interact with the crystalline lattice. This interaction causes the electron to transfer its energy to the lattice. Specifically we will be interested in the case where all of the conduction electrons per unit volume are excited by photons of energy of the order of a few ev. For n (number of conduction electrons per cc) $\sim 10^{22}$ to 10^{23} a total photon energy of the order of 10^3 to 10^4 joules per cc must be deposited in the metal.* Energy densities of this order of magnitude might conceivably be supplied by a pulsed laser beam (that is, an intense coherent light pulse).

What is ultimately desired would be to describe in detail the interaction of a pulsed laser beam with a metal upon which it impinges. Broadly speaking, such a description, if complete, would include a discussion both of the absorption of the incident radiation by the metal and the response of the metal to this deposited energy, including possible damage effects. At present such a description does not seem possible.

In the present work we separate somewhat artificially the procession of events into absorption (electron excitation) followed by electron de-excitation and lattice excitation. The validity of this approach depends on the relative magnitudes of the laser pulse length (in time) and the electron lattice relaxation time. That is, as photons

* For example, the vaporization energy of iron is $\sim \frac{1}{2}$ ev per atom (Ref. 1).

are absorbed and excite electrons to higher states, these electrons interact with the ions of the lattice and lose their energy. Grossly this is manifested in a localized heating of the metal; melting or vaporization may even result. Indeed, if such change of state begins to occur before all of the laser energy is deposited, the latter portion of the incident radiation encounters a dense high-temperature vapor (perhaps a plasma) from which it may be scattered (re-radiating energy), as well as absorbed. Thus this portion of the laser pulse may not even reach the solid metal to excite appreciable numbers of electrons. Owing to the extreme complexity of the complete process we make the somewhat idealistic assumption that the laser pulse is deposited (electrons are excited) in a time which is short compared to the electron-lattice relaxation time (which we estimate in this Memorandum^{*}).

In Section II we give the assumptions and discuss a model of a metal that is used to calculate the electron-lattice relaxation time. In Section III we compute the relaxation time, and in Section IV we discuss the results and give some numerical estimates for steel.

^{*}Some early crude experiments on steel indicate that our assumption may be reasonable.

II. MODEL FOR ELECTRON -- OPTICAL-PHONON INTERACTION

In the following we are using units with $\hbar = c = 1$ and $e^2 \cong 1/137$. We will denote the Rydberg ($me^4/2$) by R .

In the present work we assume that all of the conduction electrons per cc ($\sim 10^{22}$ to 10^{23}) in a metal have been excited by absorbing a photon of energy of the order $(1/8)R$ (corresponding to a photon wave length of $\cong 7300 \text{ \AA}$). We assume that each electron* interacts with one photon only. (In non-metallic lattices--solids with band separations large compared to the photon energy--non-linear, multi-photon processes may be very important in determining the absorption of the incident radiation; this will not be investigated here.) Before interacting with the photons the conduction electrons are assumed to be in an equilibrium Fermi distribution. That is, the electrons fill a sphere (in momentum space) up to a limiting momentum P_F (or equivalently to a limiting energy E_F).

For free electrons it is well known that $E_F \left[P_F = (2m E_F)^{1/2} \right]$ is given by

$$\left. \begin{aligned} E_F &= (1/2m)(3\pi^2 n)^{2/3} \\ &\cong (1/8)R \text{ for } n \sim 10^{22} \end{aligned} \right\} \quad (1)$$

At this point we wish to divide various metals into two classes: transition metals (e.g., Fe, Ni) and simple metals (e.g., Na, Cu). Transition metals are distinguished from simple metals by having the

*The photons will not appreciably interact with the ions because their velocities are much smaller than the electrons (the electromagnetic coupling is proportional to the current, i.e., velocity).

d shells of the constituent atoms unfilled. For example, the copper atom has a completely filled 3d shell (10 electrons) and a half-full 4s shell (one electron); the iron atom has six electrons in the 3d shell and a completely full 4s shell (two electrons). In the band theory the transition metals are characterized by having two unfilled bands, namely, a wide low-density s-electron band and a narrow high-density d-electron band* (in the simple metals the d-electron band is full). In iron, for example, the 4s-band, whose energy functions approximate those of free electrons, overlaps the 3d-band, and can take electrons from it. It can be shown, by various experiments, that there are ~ 0.1 electrons per atom in the 4s-band in iron (See Ref. 2, Chapter II, Table 2.10). In the transition metals, the Fermi level of each band is at the same height in the equilibrium state (cf. Fig. 1).

Next, consider a metal during the time when the photons are being deposited. In the simple metals the conduction electrons (s-electrons) are induced to make intraband transitions by the laser light ($\omega_{\text{laser}} = R/8 \cong 1.7$ ev). The excited s-electrons interact among themselves through their mutual coulomb interaction. The s-electrons can, to a fair approximation, be treated as free particles, each with an effective mass $\cong$ mass of a free electron. The electron-electron relaxation time in a free electron gas (of density $\sim 10^{22}$ to $10^{23}/\text{cc}$) is of the order 10^{-13} to 10^{-14} sec. Therefore, for laser pulse lengths $\gg 10^{-13}$ sec we expect that the s-electrons will be adiabatically

*The d-bands are rather narrow in energy compared to s-bands because the corresponding atomic wave functions do not spread far out in the lattice to interact strongly with neighbors.

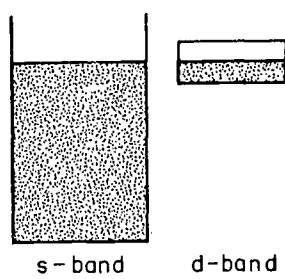


Fig.1 —Filling of levels in transition metals

heated (up to a final temperature given by the energy of the laser pulse divided by Boltzmann's constant) by the laser photons. That is, the excited electrons can be taken to be in a Fermi distribution at a temperature given by the energy in the laser pulse divided by Boltzmann's constant.

The excited electrons may now interact with the ionic lattice, giving up their energy to lattice vibrations (i.e., to phonons). In this case the dominant decay mode is known to be through acoustic phonons (see Ref. 2, Chapter 9). Electron--acoustic-phonon relaxation times are of the order 10^{-13} sec. Hence in a time very small compared with the laser pulse length (we envision laser pulses $\approx 10^{-8}$ sec) we may assume that metallic bonds are broken.*

Now consider the transition metals (e.g., Fe). Because of the unfilled d-band, electrons are able, through their counteraction with laser photons, to make interband transitions from the s-band into the d-band, as well as intraband transitions to higher states in the s-band. Electrons in excited s-band states may interact among themselves via their mutual coulomb interaction. However, because of the very high density of states in the d-band, these excited s-band electrons will

*The energy of acoustic phonons is $\omega_{\max} = K_{\max} v$, where $K_{\max}$ is $\sim \pi/\text{lattice spacing} \sim 10^{-8}$ cm, and v is the speed of sound in the metal $\sim 5 \times 10^5$ cm/sec. A typical value for $\omega_{\max}$ is ~ 0.1 ev. Generally the energies of the acoustic phonons that result from excited electrons are one or two orders of magnitude less than $\omega_{\max}$ (i.e., they have energy of the order 10^{-3} to 10^{-2} ev). Hence electrons must undergo multiple collisions with the lattice before enough energy is supplied to the lattice vibrations to break the metallic bands ($\lesssim 1$ ev per atom). Assuming it takes 10^2 to 10^3 collisions, and treating each collision as an independent event, we see that the time required for the

scatter into the d-band. Once an electron is in the d-band it is trapped, so to speak. That is, in the d-band the mutual coulomb interaction between electrons is much weaker than for s-band electrons. This is because d-band electrons are localized around the ion-core, as opposed to s-band electrons which range over the whole unit cell.

So once an electron gets into a d-band it does not interact with other electrons appreciably. Therefore, we assume that the excited electron configuration in the transition metals consists of the d-band filled as far as possible, and essentially no electrons in the s-band. In this case, electron de-excitation via acoustic phonons will not take place to any great extent. This is because if excited electrons decay to the s-band by emitting acoustic phonons (which have energies $\ll 1$ ev), these electrons (1) will interact among themselves via their mutual coulomb interaction, and (2) they will absorb acoustic phonons. Both effects thus tend to scatter the electrons back into the high density of states d-band.

On the other hand, electron de-excitation via optical phonons will result in much larger energy transfer to the lattice per collision than would de-excitation via acoustic phonons. In fact, the energies of optical phonons are on the order of an ev. That is, in a single collision (with the lattice) the excited electrons are able

metallic bands to be broken is of the order 10^{-10} to 10^{-11} sec, which is still small compared with the laser pulse length. We can therefore conclude that via acoustic phonons a simple metal becomes a high-density, high-temperature vapor in a time short compared to the laser pulse length.

to lose all of the energy given to them by the laser photons. In this case we expect that after a time of the order of the electron--optical-phonon relaxation time, the laser energy will appear as lattice vibrational energy.

Summing up, we are assuming that in the transition metals the dominant decay mechanisms for excited electrons will be through optical phonons (as contrasted to the dominant decay mechanism for excited electrons in simple metals, which is through acoustic phonons). Although the validity of this assumption can be investigated in more detail, its ultimate verification must rest with experiment.

Optical phonon transitions are the important mechanism for electron decay in dielectrics where energy gaps (of the order an ev) separate the ground state from the excited state. Although the formulas developed below apply to dielectrics, as well as transition metals, we shall give numerical estimates for steel only.

For the optical branch, the relation between energy and momentum is $\omega \approx \text{constant}$ (i.e., approximately independent of K). We take the optical branch to consist of a band of levels of energy of the order of an ev. The group velocity of an optical mode is very nearly zero.* This means that if the electrons are excited in a localized volume the optical phonons which result via electron de-excitation will stay confined to this volume. That is, there will be essentially no transport of lattice energy as there would be for acoustic modes (for which the group velocity equals v). Also, we consider the unit cell to be made up of two atoms (e.g., body-centered cubic structure).

*The center of mass of each unit cell remains fixed for optical modes.

III. CALCULATION OF ELECTRON--PHONON DECAY TIME

In this section we calculate the transition rate (probability per unit time) for the excited electrons to decay by emitting a phonon.

The hamiltonian for the system, including electron--phonon interaction but neglecting electron--electron and ion--ion interactions is

$$H = H_{\text{phn}} + H_{\text{elec}} + H_{\text{int}} \quad (2)$$

where H_{phn} is the hamiltonian for free motion of the lattice, H_{elec} is the hamiltonian for the free electrons (i.e., H_{elec} describes the motion of the conduction electrons in the periodic field of the fixed lattice)⁽²⁾ and H_{int} , in the rigid ion approximation, is given by

$$H_{\text{int}} = \sum_{L,b} V(\vec{r} - \vec{L} - \vec{Q}_{L,b}) - \sum_L V(\vec{r} - \vec{L}) \quad (3)$$

In Eq. (3) $V(\vec{r} - \vec{L})$ is the potential of the undistorted lattice at $\vec{r}$ due to atoms in the $\vec{L}$ 'th unit cell, and $\vec{Q}_{L,b}$ is the displacement from equilibrium of the b 'th atom in the L 'th unit cell. In reality, when the nucleus moves $\vec{Q}_{L,b}$, the surrounding electron core moves less. This fact is neglected in Eq. (3).

Expanding Eq. (3) in powers of Q we find

$$\begin{aligned} H_{\text{int}} = & - \sum_{L,b} \vec{Q}_{L,b} \cdot \vec{\nabla} V(\vec{r} - \vec{L}) + \frac{1}{2} \sum_{L,b} (Q_{L,b})_{\alpha} (Q_{L,b})_{\beta} \\ & \times \vec{\nabla}_{\alpha} \vec{\nabla}_{\beta} V(\vec{r} - \vec{L}) + \dots \end{aligned} \quad (4)$$

For the moment we drop all but the first term of Eq. (4). Expanding $\vec{Q}_{L,b}$ in terms of phonon creation and destruction operators (denoted by $(A_K^{\alpha})^*$ and A_K^{α} respectively) and substituting into Eq. (4) we find

$$H_{int} = i \sum_{L,b,K,\alpha} \left(\frac{1}{2M_b \omega_K N} \right)^{1/2} \left[(\Lambda_K^\alpha)^* e^{-i\vec{K} \cdot \vec{L}} + \text{complex conjugate} \right] \vec{e}_{K,b}^\alpha \cdot \vec{\nabla} V(\vec{r} - \vec{L}) \quad (6)$$

where

K is the phonon wave vector

ω_K is the frequency of the phonon of wave vector K

α is the phonon polarization direction

$\vec{e}_{K,b}^\alpha$ is a unit vector in the direction of motion of the b 'th atom for a phonon of wave vector K and polarization α

M_b is the mass of the atom located at $\vec{b}$

The first and second terms in the square brackets in Eq. (6) correspond to creation and absorption of a phonon of momentum K , respectively.

The transition probability per unit time for electrons of momentum $\vec{p}$ decaying to a state of momentum $\vec{p}'$ and emitting a phonon of momentum $\vec{K} = (\vec{p} - \vec{p}')$ is given by

$$\Gamma_1 = 2\pi |M|^2 D \quad (7)$$

where D is the density of final states per unit energy interval. For a two-particle final state D is given by

$$D = (2\pi)^3 \int \frac{d^3\vec{p}_1}{(2\pi)^3} \int \frac{d^3\vec{p}_2}{(2\pi)^3} \delta^3(\vec{p}_{in} - \vec{p}_{final}) \delta(E_{in} - E_{final}) \quad (8)$$

The matrix element between initial and final states of H_{int} is denoted by M . The initial state is an electron of momentum p , and the final state is an electron of momentum p' and a phonon of momentum K . Extracting from H_{int} (Eq. 6) the term appropriate to creation of a phonon

of momentum K (see Fig. 2) we have

$$M = i \sum_{L,b,\alpha} \left(\frac{1}{2u_K N M_b} \right)^{1/2} e^{-i\vec{K} \cdot \vec{L}} \vec{e}_{K,b}^\alpha \cdot \left(\int \psi_p^* \bar{\nabla} V(\vec{r} - \vec{L}) \psi_p d^3r \right) \quad (9)$$

The integral in Eq. (9) extends over unit volume. In Eq. (9) the ψ_p 's are the well-known Bloch wave functions for electrons in a periodic lattice. ($\psi_p = e^{i\vec{p} \cdot \vec{r}} u_p(\vec{r})$, where $u_p(\vec{r} + \vec{L}) = u_p(\vec{r})$ and $|\psi_p|^2$ integrates to unity over unit volume.) In Eq. (9) u_p corresponds to a d-band wave function and u_p , to an s-band wave function. The eigenvalue corresponding to ψ_p is $p^2/2m$, where m is an effective mass. That is, the effect of the rigid lattice on the conduction electrons is to cause a shift in their masses; otherwise the electrons behave as if they were free. In the following we take $m \sim$ free electron mass ($\cong 3.8 \times 10^4 R$).

Owing to the periodicity of the lattice, the integral appearing in Eq. (9) may be transformed as follows: The electronic wave functions must satisfy Bloch's theorem, i.e.,

$$\psi_p(\vec{r} - \vec{L}) = e^{-i\vec{p} \cdot \vec{L}} \psi_p(\vec{r})$$

Each term in the sum over L in Eq. (9) contains an integral over the whole volume. If we change the origin of the variable $\vec{r}$ in each integral to the center of the L 'th cell and then apply Bloch's theorem we have

$$M = i \sum_{L,b,\alpha} \left(\frac{1}{2u_K N M_b} \right)^{1/2} e^{-i\vec{L} \cdot (\vec{p}' + \vec{K} - \vec{p})} \times \vec{e}_{K,b}^\alpha \cdot \left(\int \psi_p^* \bar{\nabla} V(\vec{r}) \psi_p d^3r \right) \quad (10)$$

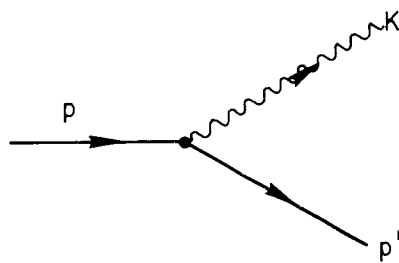


Fig.2 — Single-phonon decay

Since the integral must be the same in any cell, the sum over L may now be done. This gives us a factor N times a Kronecker delta

$\delta(\vec{K} + \vec{p}' + \vec{G} - \vec{p})$ ($\vec{G}$ is an arbitrary reciprocal lattice vector, i.e., $\vec{L} \cdot \vec{G} = \text{integer multiple of } 2\pi$). The factor N may be absorbed by assuming that the electron wave functions are now normalized to unity over the unit cell and not over unit volume as was previously done.

We have

$$M = i \delta(\vec{K} + \vec{p}' + \vec{G} - \vec{p}) \sum_{b,\alpha} \left(\frac{1}{2\omega_K N M_b} \right)^{1/2} \times \vec{e}_{K,b}^\alpha \cdot \left(\int \psi_{p'}^* \vec{\nabla} V(\mathbf{r}) \psi_p d^3\mathbf{r} \right) \quad (11)$$

Henceforth we omit the Kronecker delta, keeping in mind that in a transition we must have $\vec{p} = \vec{p}' + \vec{K} + \vec{G}$.

Now we specialize to optical phonons. For optical phonons we replace ω_K by a constant ω_0 . Summing over b we have ($\vec{e}_{K,1}^\alpha = -\vec{e}_{K,2}^\alpha \equiv \vec{e}_K^\alpha$)

$$M = i(1/2 \omega_0 N)^{1/2} (M_1^{-1/2} - M_2^{-1/2})^{1/2} \sum_{\alpha} U_{\alpha}(\vec{p}, \vec{p}') \quad (12)$$

where

$$U_{\alpha}(\vec{p}, \vec{p}') = \vec{e}_K^\alpha \cdot \int \psi_{p'}^* \vec{\nabla} V(\vec{r}) \psi_p d^3\mathbf{r} \quad (13)$$

and M_1 and M_2 are the masses of the two atoms of the unit cell.

From Eq. (12) we see that, to first order in the ionic displacements, if $M_1 = M_2$, $M \equiv 0$. This is understandable, since for optical modes the center of gravity of the unit cells remains fixed and thus the contrary motions of the atoms just balance out in their scattering

effect.* By taking into account multi-phonon processes (i.e., the effects of higher-order terms in the electron potential energy (see Eq. 4)) one obtains a non-zero contribution to M. Multi-phonon processes are discussed in the Appendix. For impure metals like steel or alloys the right hand of Eq. (12) is nonzero.

We shall now study the problem of evaluating the integral U_α defined by Eq. (13). In order to evaluate U_α we make the assumption that the potential field surrounding each ion is rigidly attached to it, and moves bodily with it.** That is, we assume that $V(r)$ can be written as a sum of atomic potentials

$$V(\vec{r}) = \sum_i V_a(\vec{r} - \vec{x}_i) \quad (14)$$

centered upon the ions at $\vec{x}_i$. Then

$$U_\alpha = - \frac{e^2}{K} \cdot \int \psi_p^* \bar{\nabla} V_a \psi_p d^3r \quad (15)$$

The integral in Eq. (15) should be carried out over the whole volume. However, it should cause little error if we take the integral over the unit cell. The potential of the bare ion does go beyond the unit cell. But the other conduction electrons tend to screen out the ionic potential beyond the unit cell.

* In the model used here (i.e., rigid ion potential with spherical symmetry round each atom) $M \equiv 0$ to first order (in phonon coordinates). In order to obtain a nonzero first-order effect it is necessary to use a model where the non-equivalence of the fields about each atom in the unit cell is taken into account.

** Calculations based upon a less restrictive assumption have been made by several authors, in particular by Bardeen (Ref. 3), but in the present state of the theory these are refinements which are of doubtful value since they only affect the numerical values of parameters which cannot in any case be calculated very accurately.

We are, in effect, using the Wigner-Seitz method⁽⁴⁾ (also known as the cellular method). In this method each atom of the lattice is surrounded by its Wigner-Seitz cell--the cell bounded by the perpendicular bisectors of the interatomic vectors (e.g., for a lattice with the body-centered cubic structure, the Wigner-Seitz cell is a truncated octahedron). The electron wave functions (for a given band) are of the form

$$\left. \begin{aligned} \psi_p &= e^{i\vec{p} \cdot \vec{r}} u_o(\vec{r}) \\ u_o(\vec{r} + \vec{L}) &= u_o(\vec{r}) \end{aligned} \right\} \quad (16)^*$$

where

and satisfies the boundary condition

$$\partial u_o / \partial n = 0,$$

$\partial / \partial n$ denoting differentiation normal to the bounding planes. Since, however, the Wigner-Seitz cells approximate closely to spheres, it is a good approximation to apply this boundary condition over the surface of a sphere of equal volume (if the radius of such a sphere is r_o , we have $4\pi r_o^3 / 3 = \text{atomic volume}$). The boundary condition thus becomes

$$\left. \frac{\partial u_o}{\partial r} \right]_{r=r_o} = 0 \quad (17)$$

Integrating the right-hand side of Eq. (15) by parts we obtain

$$U_\alpha(\vec{p}, \vec{p}') = e_K^{-\alpha} \cdot \int V_a(\vec{r}) \bar{\nabla}(\psi_p^*, \psi_p) d^3r \quad (18)$$

*The electron wave functions for different bands have the qualitative form of Eqs. (16). However, they differ quantitatively by having a different function $u_o(r)$ for each different band.

where, now, the integral is taken over a single cell. The integrated term vanishes because the integrand is periodic. Now

$$\begin{aligned}\bar{\nabla} \Psi_p &= i\bar{p} \Psi_p + e^{i\bar{p} \cdot \bar{r}} \bar{\nabla} u_0 \\ &\cong i \bar{p} \Psi_p\end{aligned}\quad (19)$$

where it is assumed that, over the greater part of the volume of the cell, $\bar{\nabla} u_0$ is negligible. Hence from Eq. (18) and (19) we obtain

$$U_\alpha(\bar{p}, \bar{p}') \cong i\bar{e}_K^\alpha \cdot (\bar{p} - \bar{p}') \int V_a(\bar{r}) \Psi_{p'}^* \Psi_p d^3r \quad (20a)$$

$$= i\bar{e}_K^\alpha \cdot (\bar{K} + \bar{G}) \int V_a(\bar{r}) \Psi_{p'}^* \Psi_p d^3r \quad (20b)$$

where we have used conservation of quasi-momentum in obtaining Eq. (20b) from Eq. (20a).

Now, Ump-Klapp processes (i.e., processes for which $G \neq 0$) are responsible for scattering of electrons through angles greater than $2 \sin^{-1}(2^{-2/3}) \cong 79^\circ$.⁽³⁾ Here, electrons will be scattered through angles less than 1 rad. ($\sim 57^\circ$). Henceforth we take $\bar{G} = 0$. Conservation of momentum now reads

$$\bar{p} = \bar{K} + \bar{p}' \quad (21)$$

With $\bar{G} = 0$ the initial factor in Eq. (20b) becomes $\bar{e}_K^\alpha \cdot \bar{K}$. This indicates that only longitudinal phonons will interact with electrons.*

In order to estimate the integral in Eq. (20b) we argue as follows: If, for the moment, we take $\bar{p} = \bar{p}'$ (i.e., consider an intraband transition with $\bar{K} = 0$) then we require the mean value of the potential energy over

*For processes with $\bar{G} \neq 0$ transverse phonons may interact with electrons. For then there is no guarantee that $\bar{K} + \bar{G}$ is parallel to $\bar{K}$.

the unit cell. The magnitude of the mean value of the potential energy is of the order of the average electron kinetic energy, which is of the order of the Fermi energy. On the other hand, consider the value of the integral for large K . Due to shielding (by other conduction electrons) $V_a(r) \cong 0$ for values of r greater than the order of the interatomic distance. Hence the integral vanishes (because the integrand contains the function $e^{i\vec{K} \cdot \vec{r}}$ which oscillates rapidly for large K).

Here, $Kr \lesssim 1$ which is intermediate between very small and very large K . Also, we require the value of the integral for Ψ_p describing a d-band, and for Ψ_p , describing a s-band (i.e., we want the value of the integral for an interband transition). In this case, the initial and final wave functions contain different angular dependencies, which, on integration will tend to reduce the value of the integral. Hence, we expect that the value of the integral is less than E_F (perhaps a fraction $\lesssim 1$ of E_F). To determine exactly how much less we would have to determine a realistic potential $V(r)$ that describes correctly the properties of the metal, substitute this potential into a Schrodinger equation that includes electron-electron interactions (so as to include screening), determine the electron wave functions and then substitute the potential and wave functions into the integral. This, however, is beyond the scope of the present work. Furthermore, since $Kr \lesssim 1$, we see no reason to assume that the integral is a very sensitive function of K . Therefore, we take the value of this integral to be independent of K , and of magnitude approximately $E_F = R/8$.

From what has just been said, we have

$$\begin{aligned} U_{\alpha}(\bar{p}, \bar{p}') &= iKI \text{ for longitudinal modes} \\ &= 0 \text{ for transverse modes} \end{aligned} \quad (22)$$

where $I \cong R/8$.

From Eqs. (22), (12), (8), and (7) we have

$$\begin{aligned} \Gamma_1 &= 2\pi |M|^2 D \\ &= (M_1^{-1/2} - M_2^{-1/2})^2 (I^2/2 \omega_0 N) \int \frac{d^3 K}{(2\pi)^3} K^2 \delta \left(\epsilon_d(p) - \frac{(\bar{p} - \bar{K})^2}{m_s} - \omega_0 \right) \end{aligned} \quad (23)$$

where ω_0 is the phonon energy.

In arriving at Eq. (23) we have used conservation of momentum (Eq. (21)) and integrated over the final electron momentum (using the delta function of momentum that appears in Eq. (8)). Here, all of the excited d-electrons (of energy $\epsilon_d(p) = \frac{p^2}{2m} + V_d$, where V_d is the average potential energy of a d-electron) are taken to be in a narrow region beginning at $E_F = R/8$. The final energy is an s-band electron (of energy $(\bar{p} - \bar{K})^2/2m$), and an optical phonon of energy ω_0 (which is independent of K). Choosing the polar axis along $\bar{p}$ and then integrating over the azimuthal angle we find*

$$\Gamma_1 = (M_1^{-1/2} - M_2^{-1/2})^2 (I^2/4\pi \omega_0 N) \int_{-1}^1 dx \int K^4 dK \delta(\bar{p} \cdot \bar{K}/m - (K^2/2m) - \omega) \quad (24)$$

where $x = \cosine$ of the angle between $\bar{p}$ and $\bar{K}$, and $\omega = \omega_0 + \frac{p^2}{2m} - \epsilon_d(p)$.

Integrating over K we find

$$\begin{aligned} \Gamma_1 &= (M_1^{-1/2} - M_2^{-1/2})^2 (I^2/4\pi \omega_0 N) p^3 \int_a^1 \frac{dx}{(x^2 - a^2)^{1/2}} \\ &\quad \times \left[\left(x + \sqrt{x^2 - a^2} \right)^4 + \left(x - \sqrt{x^2 - a^2} \right)^4 \right] \end{aligned} \quad (25)$$

* Hereafter we drop the subscript s on m .

where

$$a^2 = 2m \omega / p^2 \quad (26)$$

The lower limit on the integral in Eq. (25) comes from the requirement that K be real.

The integration over x is elementary. The final result is

$$\Gamma_1 = C p^3 (1 - a^2)^{1/2} (1 - a^2/2) \quad (27)$$

where

$$C = (M_1^{-1/2} - M_2^{-1/2})^2 (mI^2 / \pi \omega_0 N) \quad (28)$$

Now,

$$\begin{aligned} \omega &= \omega_0 + \frac{p^2}{2m} - \epsilon_d(p) \\ &= \omega_0 + \frac{p^2}{2m} - \left(\frac{p^2}{2m} + V_d \right) \\ &= \omega_0 - V_d \end{aligned} \quad (29)$$

Substituting Eqs. (28) and (29) into Eq. (27) we find

$$\Gamma_1 \cong C p_F^3 \quad (30)$$

In obtaining Eq. (30) we have taken $\omega_0 \sim V_d \sim E_F$, and $p \sim p_F$. In the next section we discuss Eq. (30), giving some numerical estimates for steel.

IV. DISCUSSION AND CONCLUSIONS

Let us apply Eq. (30) to stainless steel (≈ 90 per cent Fe, 10 per cent Cr). In this case we assume that 20 per cent of the unit cells contain a Cr atom.^{(6)*} Therefore, the interaction amplitude (Eq. (11)) should contain a factor 2×10^{-1} and the transition probability a factor 4×10^{-2} . Upon substituting the Fe and Cr mass into Eq. (30) we have (we take $m_0 = 1/8 R$, $2N \sim 10^{23}$ cells/cc, $m = 3.8 \times 10^4 R$, $I = E_F = R/8$)

$$\Gamma_1 = 1/\tau_1 \approx 2 \times 10^{-10} R \quad (31)$$

Now,

$$R \approx 2 \times 10^{16} \text{ sec}^{-1}$$

Hence,

$$\tau_1 \approx 2.5 \times 10^{-7} \text{ sec (stainless steel)} \quad (32)$$

For a steel that is predominantly 90 per cent Fe and 10 per cent Ni we find

$$\tau_1 \approx 1.5 \times 10^{-6} \text{ sec (Fe-Ni steel)**}$$

Physically, in time τ_1 an excited electron has a probability of ≈ 37 per cent (i.e., e^{-1}) of decaying by emitting a phonon (i.e., the square of the electron wave function contains a factor $e^{-\Gamma_1 t}$). In a few times τ_1 all of the electrons should have decayed and hence the

*Cells (80 per cent) that contain two Fe atoms contribute zero to the amplitude (see Eq. (28)).

**For a 50-50 Fe-Cr alloy $\tau_1 \sim 1 \times 10^{-8}$ sec; for a 50-50 Fe-Mo alloy $\tau_1 \sim 10^{-10}$ sec.

lattice gains energy of the order of the laser energy (here taken $\sim 10^3$ to 10^4 joules per cc).^{*} Hence, at the end of this time the lattice energy will be greater than the vaporization energy, which implies that the metallic lattice has become a fluid. This fluid being at a very high density and temperature ($\sim 10^4$ to 10^5 K) will expand, causing large pressure gradients (i.e., shocks) etc.

We should like to point out that the time obtained here is much longer than the time it would take if the electrons interact with photons whose energy $\gg R$ (e.g., X-rays). In this case the wavelength of the excited electron is much smaller than the interatomic spacing and the velocity of the electrons $\sim 10^8$ cm sec⁻¹. The electron makes collisions with atoms, giving up energy to the atoms. Since for iron the vaporization energy (per atom) is $\sim 1/2$ ev, it will take few (say, 10) collisions (per electron) before the metallic bonds are broken. The time in which this happens is of the order of the mean free path ($\sim 10^{-6}$ cm)^{**} divided by the velocity of the electron

^{*} In the Appendix we show that the transition probability for an electron decaying by emitting two phonons is, for stainless steel, an order of magnitude less than for single phonon emission. However, for Fe-Ni steel, the first and second order transition probabilities are of the same order of magnitude. This result is quite accidental since in the first-order transition probability for steel there occurs the difference of two nearly equal numbers and a small factor (4×10^{-2}) which takes into account that 20 per cent of the unit cells give a non-zero scattering effect. The first-order transition probability for most alloys is typically much larger (decay time much shorter) than for steel (e.g., for a 50-50 Fe-Mo alloy $\tau_1 \sim 10^{-10}$ sec) and hence the first-order scattering dominates (second-order decay times are typically $\sim 10^{-6}$ sec).

^{**} The mean free path $= (n\sigma)^{-1}$, where the absorption cross-section σ , for Fe, can be taken (at X-ray energies) to be the geometric cross-section of the Fe atom ($\sigma \approx 10^{-16}$ cm²). Hence, for $n \sim 10^{22}$, $(n\sigma)^{-1} \approx 10^{-6}$ cm.

($\sim 10^8$ cm/sec). That is, this time (for ten collisions) is of the order of 10^{-13} sec.

Also, we note the manner in which a metal breaks up is similar to the X-ray case when the laser photon density (per electron) is much greater than one. For, when the photon density (per electron) is much larger than 1, the electron picks up (on the average) energy much larger than the Fermi-energy (i.e., in this case multiphoton absorption takes place) or equivalently, momentum much larger than the Fermi-momentum. That is, in this case the wavelengths of the excited electrons are much less than the interatomic spacing. These conditions are the same as the X-ray case.

We restate that optical-phonon decay is the principal mechanism by which substances with band gaps ($\geq \omega_{\text{laser}}$) de-excite (e.g., dielectrics and insulators). Where the gap spacing is much larger than the laser photon energy, the material will be transparent to the laser beam unless the average energy given to the valence electrons is $\geq$ gap spacing (i.e., we would expect the material to be transparent unless the laser photon density (per electron) is large compared to 1, so that the electron may undergo multiple photon absorption). For further information on multi-photon absorption see Ref. 7.

We emphasize that here we have calculated the redistribution of excited electrons with accompanying phonon excitation under highly non-equilibrium conditions. Only when the photon energy is deposited in a time which is longer than the electron-phonon decay time ($\sim 10^{-7}$ to 10^{-6} sec for steel) is it meaningful to think of the metal as being vaporized instantaneously. Hence, for steel and with laser pulse lengths $< 10^{-7}$ sec it is not possible to apply immediately an equilibrium equation of state to determine pressure gradients, etc. It is necessary to

wait a time of the order of the electron-phonon decay time before such calculations become meaningful.

Finally, we re-emphasize that our conclusions about the decay mechanism of transition metals depend completely on the validity of the assumption of the "d-band trap" (i.e., the assumption that the conduction electrons become inhibited from decaying via acoustic-phonons because of their affinity to stay in the high-density of states d-band). If this assumption is valid then we conclude that in the transition metals the electron de-excitation will take place (via optical-phonons) in a time $\sim 10^{-7}$ to 10^{-6} sec as contrasted to the simple metals where electron de-excitation takes place (via acoustic phonon) in a time $\sim 10^{-11}$ to 10^{-10} sec. With laser pulse lengths $\sim 10^{-8}$ sec and fast photo-detectors (with resolving time $\sim 10^{-9}$ sec) it is conceivable that experimental investigation of the early time history of the metallic decomposition in the transition metals may be done.

Appendix

TWO-PHONON DECAY

In this appendix we estimate the decay rate into two phonons. Two-phonon final states come about in two different ways (see Figs. 3 and 4).

First consider the process depicted in Fig. 2. The amplitude for this process arises out of the second-order expansion of the electron potential energy. Now,

$$\Gamma_2 = 2\pi |H_{int}^{(2)}|^2 D^* \quad (34)$$

where, from Eq. (4),

$$H_{int}^{(2)} = \frac{1}{2} \sum_{L,b} (Q_{L,b})_{\alpha} (Q_{L,b})_{\beta} \nabla_{\alpha} \nabla_{\beta} V(\vec{r} - \vec{L}) \quad (35)$$

and

$$D = (2\pi)^3 \int \frac{d^3 p_1}{(2\pi)^3} \int \frac{d^3 p_2}{(2\pi)^3} \int \frac{d^3 p_3}{(2\pi)^3} \delta^3(\vec{p}_{in} - \vec{p}_{out}) \delta(E_{in} - E_{out})^{**} \quad (36)$$

Expanding the Q's in terms of phonon creation and annihilation operators, and retaining those terms that correspond to the creation of two phonons, we find

$$\begin{aligned} \eta_2 = -\frac{1}{2} \sum_{b,\alpha} \left[\left(\frac{1}{2NM_b \omega_K} \right)^{1/2} \left(\frac{1}{2NM_b \omega_{K'}} \right)^{1/2} \tilde{e}_{K,b}^{\alpha} \tilde{e}_{K',b}^{\alpha} \right. \\ \left. \int \psi_{p'}^* \bar{\nabla} \bar{\nabla} V(\vec{r}) \psi_p d^3 r \right] \times \delta(\vec{p} - \vec{p}' - \vec{k} - \vec{k} - \vec{G}) \end{aligned} \quad (37)$$

* We denote $(H_{int})_{if}$ by η_2 .

** Here we are dealing with a three-particle final state.

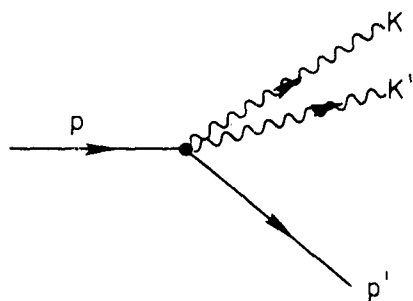


Fig.3 — Double-phonon decay

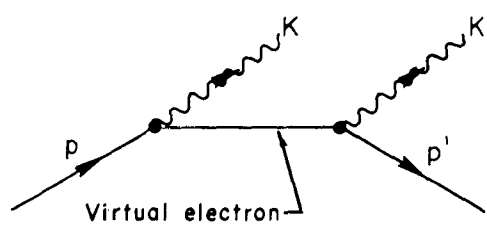


Fig.4 — Two successive virtual single-phonon decays

In obtaining Eq. (37) we have performed the summation over L (see the derivation of Eq. (10) for details).^{*} Assuming a representation for $V(r)$ such as in Eq. (14) we have to evaluate integrals of the form:

$$\int \Psi_p^* \bar{\nabla} \bar{\nabla} V_a(r) \Psi_p d^3r \quad (38)$$

Where the integration is performed over only the unit cell. Integrating Expression (38) twice by parts we obtain

$$(\bar{K} - \bar{K}') (\bar{K} - \bar{K}') \int V(\bar{r}) \Psi_p^* \Psi_p d^3r^{**} \quad (39)$$

The integrated terms are zero because the integrands are periodic over the lattice. The integral appearing in Expression (39) is identical to the integral I discussed in Section III (see discussion preceding Eq. (22)).

For optical modes Eq. (37) yields (on performing the summation over b)^{***}

$$\eta_2 = - (I/2N \omega_0) (1/M_1 + 1/M_2) \sum_{\alpha} \bar{e}_K^{\alpha} \cdot (\bar{K} - \bar{K}') \bar{e}_{K'}^{\alpha} \cdot (\bar{K} - \bar{K}') \quad (40)$$

Some qualitative features of the second-order amplitude may be seen from Eq. (39). First, if $M_1 = M_2$ we see that $\eta_2 \neq 0$. We have seen that the first-order term vanishes if $M_1 = M_2$ (see the discussion following Eq. (13)). Here, the ionic displacements appear quadratically and thus the scattering amplitude from each ion in the unit cell has

^{*}The electron wave functions are assumed to be normalized to unity in the unit cell.

^{**}As before, we neglect processes where $\bar{G} \neq 0$.

^{***}We have arbitrarily set $\omega_{K'} = \omega_K = \omega_0/2$ where $\omega_0 \sim (1/8)R$.

the same relative sign. In pure metallic crystals (e.g., pure Fe) the first non-vanishing contribution to the decay rate comes from the second-order term in the expansion of the electron potential energy. In order to compare this second-order rate with the first-order rate for steel we put $M_1 = M_2 =$ mass of the Fe atom (since Fe is the major constituent of steel). Second, we see that, in the second order, transverse phonons will couple.* Here, however, since we are interested only in an order of magnitude estimate, we shall neglect the contribution to the decay rate arising from transverse phonons. With these simplifications Eq. (40) becomes

$$\eta_2 = - (I/NM \omega_0) (\bar{\mathbf{K}} \cdot (\bar{\mathbf{K}} + \bar{\mathbf{K}}')/K) (\bar{\mathbf{K}}' \cdot (\bar{\mathbf{K}} + \bar{\mathbf{K}}')/K') \quad (41)$$

Upon substituting Eqs. (36) and (41) into Eq. (34) we find

$$\begin{aligned} \Gamma_2 = (I/NM \omega_0)^2 \int d^3K d^3K' / (2\pi)^5 \left\{ \delta(\epsilon_d(p) - [(\bar{\mathbf{p}} - \bar{\mathbf{K}} - \bar{\mathbf{K}}')^2/2m] - \omega_0) \right. \\ \left. \times (K \cdot (\bar{\mathbf{K}} + \bar{\mathbf{K}}')/K)^2 (\bar{\mathbf{K}}' \cdot (\bar{\mathbf{K}} + \bar{\mathbf{K}}')/K')^2 \right\} \end{aligned} \quad (42)$$

where the upper limit on these integrals is $\sim K_{\max}$ ($K_{\max} \sim \pi/\text{lattice spacing}$). Changing from the variables $\bar{\mathbf{K}}, \bar{\mathbf{K}}'$, to $\bar{\mathbf{K}}, \bar{\mathbf{Q}}$ ($\bar{\mathbf{Q}} = \bar{\mathbf{K}} + \bar{\mathbf{K}}'$) and using conservation of momentum to express $\bar{\mathbf{K}}' \cdot \bar{\mathbf{Q}}$ and K'^2 in terms of $\bar{\mathbf{Q}}$ and $\bar{\mathbf{K}}$ we find

$$\begin{aligned} \Gamma_2 = \left[1/(2\pi)^5 \right] (I/NM \omega_0)^2 \int d^3Q \delta(\bar{\mathbf{p}} \cdot \bar{\mathbf{Q}}/m - Q^2/2m - \omega) \\ \times \int d^3K (Q^2 - \bar{\mathbf{Q}} \cdot \bar{\mathbf{K}})^2 (\bar{\mathbf{Q}} \cdot \bar{\mathbf{K}})^2 / K^2 (Q^2 + K^2 - 2\bar{\mathbf{Q}} \cdot \bar{\mathbf{K}}) \end{aligned} \quad (43)$$

where ω is given in Eq. (29).

* Since, in general, $\bar{\mathbf{K}} - \bar{\mathbf{K}}'$ is not parallel to $\bar{\mathbf{K}}$ or $\bar{\mathbf{K}}'$.

In order to obtain an order of magnitude estimate of the K integrate in Eq. (43) we take $\vec{Q}$ parallel to $\vec{K}$. With this we find

$$\int d^3K \frac{(Q^2 - \vec{Q} \cdot \vec{K})^2 (\vec{Q} \cdot \vec{K})^2}{K^2(Q^2 + K^2 - 2\vec{Q} \cdot \vec{K})} \approx Q^4 \int d^3K = \frac{4\pi}{3} K_{\text{Max}}^3 Q^4 \quad (44)$$

By substituting Eq. (44) into Eq. (43) and performing the Q integral by means of the delta function we find

$$\begin{aligned} \Gamma_2 &= \frac{2m K_{\text{max}}^3}{15(2\pi)^3} (I/NM \omega_0)^2 p^5 \int_a^1 \frac{dx}{(x^2 - a^2)^{1/2}} \\ &\times \left[\left(x + \sqrt{x^2 - a^2} \right)^6 + \left(x - \sqrt{x^2 - a^2} \right)^6 \right] \end{aligned} \quad (45)$$

where

$$a^2 = 2m \omega/p^2 \quad (46)$$

The lower limit on the integral in Eq. (45) comes from the requirement that K be real. The integration over x is elementary. The final result is

$$\Gamma_2 = \frac{4m}{3} \frac{K_{\text{max}}^3}{(2\pi)^3} (I/NM \omega_0)^2 p^5 (1 - a^2)^{1/2} (16/3 - (16a^2/3) + a^4) \quad (47)$$

Putting M = mass Fe atom and $K_{\text{max}} \sim 100$ R we find

$$\Gamma_2 \sim 3 \times 10^{-11} \text{R}$$

or

$$\tau_2 = 1/\Gamma_2 \sim 10^{-6} \text{sec} \quad (48)$$

Next, consider the process shown in Fig. 3. That is, double phonon emission by two successive first-order emissions, each of which

is characterized by an amplitude given by Eq. (12). When the electron in the intermediate state is nearly free, the two successive emissions are essentially independent of each other (i.e., this case is essentially multiple single-phonon emission, and should not, strictly speaking, be thought of as double-phonon emission). In this case we expect the decay rate to be of the same order of magnitude as Γ_1 .

On the other hand, when the electron in the intermediate state is highly virtual the situation is quite different. For example, $E_{in} - E_{int} \sim E_F$, where E_{in} is the energy of the electron in the initial state, and E_{int} is the energy of the phonon (which is in a free state) and electron (which is in a virtual state) in the intermediate state. In this case an order of magnitude estimate for this decay rate is $\sim \Gamma_1^2/E_F \sim 10^{-18}$ R. This rate is many orders of magnitude less than Γ_2 .

In Section IV we have seen that for steel $\tau_1 \sim 10^{-7}$ sec ($\tau_2/\tau_1 \sim 10$). Thus we conclude that double-phonon emission will be important only when we are dealing with a very pure metal (not an alloy, since for a typical alloy the unit cell contains atoms with not too small mass differences--compared, say, with steel--and hence Γ_1 will dominate).

Lastly we emphasize that the calculation of Γ_2 is, at most, very crude since we have even less knowledge of the second derivative of the electron potential energy than we have of its first.

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