

*Section VI. Collision cascades, radiation damage and ranges*

**ENERGY TRANSFER BETWEEN ELECTRONS AND IONS IN COLLISION CASCADES IN SOLIDS**

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This paper attempts an overview of the mechanisms, rates, and characteristics of the several processes by which electronic and ionic energy exchange can occur. This energy exchange raises questions about widely accepted assumptions, and the circumstances in which those assumptions must be questioned. The situations where the problems are most easily seen concern low energies, and especially topics such as whether there is a threshold associated with a band gap or situations where structural or chemical features can be affected by the energy transfer. Yet there are other cases in which ion/electron energy transfer could be important, such as in the highly excited centre of a cascade. In such situations, the observable consequences may be harder to relate to the energy exchange. The issue is therefore one of the final state achieved (and hence affected by annealing of defects and various thermal processes) as opposed to the higher-energy phenomena themselves. I discuss the role of the electronic system in metals as an energy sink and a means of energy transport, drawing analogies with the better-understood insulators. There are strong hints of electronic effects in collision cascades, but their status is still not clear.

**1. Introduction**

In the classic study by Lindhard and his co-workers [1] one finds a systematic series of basic approximations A–E'. These contain the essential physics of the role of electrons in atomic collisions, i.e. the extent to which one must go beyond simple "billiard ball" models of the collision process. These assumptions form the basis of the conventional wisdom, and their relevance and value has been supported by many studies. I shall start by listing these assumptions, since they provide a framework for any substantial analysis.

(A) *Electrons produced in collision cascades do not produce recoil atoms with appreciable energies.* This assumption about electrons generated in collision cascades has its origins in the classical dynamics of particles with very different masses, like electrons and nuclei. Certainly it is true – and recognized by Lindhard – that there can be processes loosely described as chemical which lead to ion energies of a few eV. Only the proponents of cold fusion have suggested that far larger energies are possible, and such phenomena, even if true, would not concern us in the present meeting.

(B) *Atomic bindings.* Atomic binding (again chemical energies, of the order of a few eV) can be ignored for heavy particles at the energies for which electronic stopping has appreciable influence. The recent analysis of core and bond stopping powers in compounds shows very substantial differences between single, double and triple bonds between carbons; to what extent this is general is unclear. The corollary is that there are lower-energy regimes (125 keV protons in the case cited) for which atomic binding has significance. In such circumstances, the binding needs careful definition in rela-

tion to whether the process is adiabatic, and whether there are any irreversible components through other excitations.

(C) *Energy transfers to electrons are relatively small.* The losses of energy can be regarded as the sum of many small losses in individual collisions. Here again there will be problems if there is a threshold such that electronic excitation needs a finite energy. For metals, there are always excitations possible with infinitesimal energy (though sometimes quantum effects emerge when unexpected [3]), and the implications for collisions have yet to be investigated. For semiconductors and insulators, the minimum excitation energy (for no free carriers, extrinsic or intrinsic) is the band gap. Despite early proposals that the band gap should provide some sort of threshold (e.g. that the band gap might be a minimum displacement energy), experiment does not seem to confirm such proposals (see section 2.6). Moreover, the energy needed to create an electron–hole pair is observed to be substantially above the band gap energy; typically [4] three band gaps of energy were needed to generate a pair, emphasising the need for careful energy definitions noted above.

(D) *Electronic and nuclear collision contributions to energy loss can be separated.* This is one of several *superposition* assumptions used. For electrons, the large number of "weak" collisions, often with large impact parameters, coupled with the lack of ion displacements by the scattered electrons, are among the factors here. Yet one can envisage cases where the effects are not additive. For example, if the electrons cause a permanent change in the solid – e.g. a phase change to a solid of different composition or density, or if, in an insulator, electric fields are built up – then the subsequent

nuclear scatter could be affected. Some examples are noted in section 3.

Assumptions E and E' of ref. [11] need not concern us at present.

## 2. Aspects of the standard picture

The standard picture is usually the high-energy regime (here meaning that the projectile kinetic energy is such that detailed energy levels of target and projectile can be incorporated in some simple model), in which a projectile of mass  $M_1$  and with atomic number  $Z_1$  is incident on a solid with  $N$  atoms per unit volume, each of mass  $M_2$  and atomic number  $Z_2$ . Note that the standard picture only recognises a *number density*  $N$  of atoms. The crystal structure cannot be ignored always – channelling is a good example – but other cases may arise when projectile energies are low enough for the chemistry of the target to play a role. Whilst the energy loss at high projectile energies is dominated by electronic losses, rather than nuclear, what happens to the electrons after collisions is deemed unimportant, and indeed it is hard to identify consequences of energy transfer from ions to electrons in this regime.

### 2.1. Standard forms

The energy loss is often expressed in a standard simple form which we may use to ask where the consequences of ion–electron energy exchange might be identified:

$$dE/dR = - \frac{4\pi(Z_1e)^2 e^2 N Z_2}{m v_1^2} L,$$

where  $L$  has been obtained in various approximations, e.g.

$$L = \ln(2mv_1^2/I),$$

for  $I \ll 2mv_1^2$ ,  $I$  being the mean excitation energy for the target in its ground state, usually defined from the dipole oscillator strength for the ions supposed to make up the solid. Sigmund [5] has reviewed various generalisations of this approach. The main features in all such discussions is a stopping power approximately proportional to  $v$  in the collision cascade regime. There is a peak in the stopping power as a function of  $(2mv_1^2/I)$ . Interaction of projectile and solid is greatest at the peak; loss of energy to electrons is increasingly important at higher projectile energies. Yet in both these regimes (i.e. at the peak and above) the electrons play a largely passive role, e.g. by providing an interatomic potential and a polarisable medium (and hence, of course, an energy sink).

Issues arising are these:

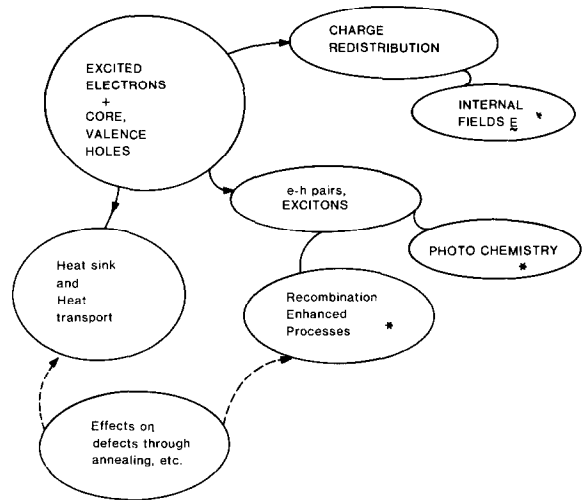


Fig. 1. Consequences of energy given by cascade ions to the electronic system. Features marked \* are mainly relevant in nonmetals.

(1) What happens at the lowest projectile velocities? Is there a regime in which the band structure of the solid becomes important, or for which the details of the electron density matter? Low ionic velocities are important for displaced target atoms and especially near the edges of a cascade.

(2) How good is the assumption that the different atoms or ions in the solid simply have superposing contributions to the energy loss? Exceptions seem largest for low atomic numbers, e.g. hydrocarbons [2]; as another case, recent tests of the Bragg–Kleeman [7] effect show significant deviations only for the low-atomic-number compound BeO at lower (0.5–0.7 MeV/amu) energies.

(3) Do the electrons do anything else but act as a sink through their single-particle excitation (kinetic energy)? Here we must consider both mechanisms of energy transfer by the electronic system and the way in which excited electrons can induce nuclear motions. In addition to these broad issues of electrons as an energy sink and in energy transfer, we shall need to consider how rapidly electrons thermalise. Can we sensibly define a temperature  $T_e$  for the electrons, distinct from the ambient temperature  $T_B$  and some locally “hot” ion temperature  $T_L$ ? This question is addressed in section 4. We may also identify three special topics (see fig. 1) which will be discussed in later sections:

- Charge redistribution, leading to internal fields. This is additional to charging from surface losses of electrons.
- Generation of electron–hole pairs and of excitons in nonmetals, leading (through energy localisation) to photochemical and enhanced diffusion processes.
- Plasmon generation in metals or nonmetals and

other electronic excitations which affect the efficiency of the electron gas as a means of retaining and transferring energy.

## 2.2. Energy densities and time scales

We shall need to know the relative orders of magnitude of the energies, e.g. the maximum effective ionic temperature at the centre of a cascade and the energies of the various excitations of the electronic system. We may get a scale for values by looking at specific results [8,9]. Some general results can be obtained by simple arguments for the class of potentials characterised by Lindhard's parameter  $m$  [1]. In particular, if  $R(E)$  is the path length, the deposited energy spread is characterised by [8]

$$[\langle x^2 \rangle - \langle x \rangle^2]^{1/2} = (1 + 4m)^{-1/2} [2m/(1 + 2m)] R.$$

The initial energy  $E$  is thus distributed over a volume proportional to  $R^3$ , the proportionality constant being a function of  $m$ . Since  $R$  varies as  $E^{2m}$ , we expect the energy density to scale as  $E/(E^{2m})^3$ , i.e. as  $E^{1-6m}$ . One key parameter is  $\theta$ , defined as  $\theta$  = [energy per target atom]. Clearly  $\theta$  can be regarded as a measure of local temperature, and varies in space, having a maximum value  $\theta_0$  given by  $\theta_0 = G(m)N^2/E^{g(m)}$  in which  $g(m) = (6m - 1)$  is 1 for  $m = 1/3$  and 2 for  $m = 1/2$ , in agreement with the scaling above. This maximum  $\theta_0$  can vary enormously from case to case, and is especially large when both target and projectile masses are large. For 10 keV Te<sup>+</sup> on Ar [9], the maximum value of the mean target atom energy is about 10 eV, i.e. above the stronger chemical energies (1–2 eV) and close to electronic excitation energies, both of single particles and collective (plasmon) excitations.

A timescale is also needed. However, there are at least three time scales [9]. (I shall define others later, involving electrons.) The first time scale is the slowing-down time of the projectile,  $\tau_0$ . The second time scale describes how rapidly the recoil atoms dissipate their energy,  $\tau'$ . Clearly this is related to how fast a local ionic temperature might be set up. Finally, there is a relaxation time  $\tau$  for  $\theta_0$ , which describes how fast the more energetic host atoms lose their energy. This third time scale includes a thermal conduction component, which Sigmund discusses using kinetic theory (i.e. excluding electronic contributions). Clearly, there are other possible characteristic times, such as those (related to  $\tau'$  and  $\tau$ ) which determine how fast thermodynamic equilibrium is set up (these will become important in section 4) but the three just defined characterise much of the standard behaviour. Sigmund's results for Te on Ar show that  $\tau_0$  varies rather slowly with projectile energy, and that the projectile slows down typically in a few tenths of a picosecond. The relaxation time for  $\theta$  is

longer, typically  $\tau \sim 1$ –10 ps, though it decreases as the projectile energy falls.

One feature of this analysis which will be important later is that there is no strong variation in behaviour expected from, say, Ni to Cu targets and comparable projectile masses and energies. When differences are observed to be large, we realise other explanations are necessary [10]. It is here that signs of electronic effects will emerge.

## 2.3. Behaviour at very low energies: Are there threshold effects?

At very low projectile energies, or in any region where all ionic kinetic energies are comparable with the chemical and structural energies, one expects there will be dependences on features like crystal structure and bonding, and on the projectile energy relative to core excitation energies. Yet one might hope that, for metals at least, the dominant controlling parameters would be rather simple, such as the average valence electron density. This question has been looked at systematically [11] for different ions incident on metals. Their data compilation also allows an assessment of several of the stopping power expressions.

At the centre of the analysis lie two ideas. First, the average electron density can be estimated from experimental plasmon data. This allows us to use a dimensionless parameter which gives the radius  $r_s$  in atomic units of the sphere containing one electron. The same parameter also defines the Fermi velocity for a free-electron gas. The second idea concerns the relative velocities of the several particles. In particular, on the projectile, only those electrons with an orbital velocity above some identified threshold are assumed to remain bound; allowance must be made for the dependence on  $r_s$  of the relative electron/ion velocities when the projectile is only moving at a fraction of the Fermi velocity.

The conclusions which emerge are these. First, proton stopping powers do indeed seem to depend predominantly on the average electron density. Secondly, for heavier ions, there is only a weak material dependence, provided (1) the data are compared with proton data and (2) the  $r_s$  dependence of relative electron velocities is allowed for, and an appropriate effective charge fraction for the projectile is estimated systematically. This systematic dependence can be represented by a universal function.

At the very lowest projectile velocities (ion velocities less than the electronic Fermi velocity) the stopping power is related to the extra resistivity which would be caused by the stationary ion. In a uniform electron gas, it is clearly equivalent to have electrons moving, scattered by a stationary ion (the resistivity problem) or the ion moving through a steady distribution of elec-

trons (the stopping problem). This issue has been addressed in refs. [12–14]; the basic result is that  $-dE/dx$  is proportional to  $\Delta\rho$  and to the ion velocity. This relation is helpful in generalising molecular dynamics models (see section 4).

The situation here is therefore that, for metals, subject to simple generalisations regarding projectile charge, the behaviour is dominated by the electron density. What is not checked is whether the behaviour is different when there is a discrete finite excitation energy, as in insulators where there is a band gap. I shall turn to that issue later, but note that the situation of a finite gap can be treated in another useful, if ideal, case.

#### 2.4. Universal Damage Models

The behaviour for low ion energies described in section 2.4 is an example of a Universal Damage Model, by which I mean a model in which behaviour over a wide range of circumstances can be described within a single picture. Many of the analytical theoretical descriptions propose universal models (Thomas–Fermi theory can be regarded as such a case, though many are simpler); when experiment confirms them, these experiments are verifying universal models to some degree. Often Universal models are models of simple systems, so it is worth noting a case when very complex metallic system show universal behaviour and where it is likely that energy exchange between ions and electrons is important in what happens. An example comes from the field of high-temperature superconductivity. Here it is found that [15], over a very wide range of irradiation circumstances, there is a simple relation between the damage (as measured by  $d(\Delta T_c)/d\phi$ ) and the non-ionizing energy deposition. The natural conclusion is that there is a single mechanism and, for these 1:2:3 superconductors, the mechanism is presumably oxygen sublattice disorder. Whilst there is also secondary damage (e.g. from new phases which need Cu motion too) the main damage mechanism is concentrated on one sublattice. This shows parallels with behaviour in ionic and semiconductor systems, as noted later.

#### 2.5. Finite excitation energies

The analysis of Bethe theory for a harmonic oscillator is of interest for several reasons. It gives some helpful analytic limits; it solves a case for which the oscillator frequency provides a characteristic excitation energy; in addition, though I shall not pursue this here, it provides a technique for calculating (mechanical) friction coefficients.

Sigmund and Haagerup [16] calculate the stopping number  $L$  in several limits. For heavy projectiles,  $L$  is characterised by a parameter  $\epsilon = [\text{oscillator energy}]/[2mv_1^2]$ , with  $m$  the electron mass and  $v$  the projectile velocity.

Among the points to emerge are these. First, for slow heavy projectiles, i.e. for large  $\epsilon$ , the stopping number  $L$  varies thus:  $L \sim \exp(-\epsilon)/2\epsilon$ . Secondly, the predictions can be compared with those for the kinetic theory of stopping, when the process is regarded as binary collisions with free target electrons rather like the model in section 2.3. At low speeds, the kinetic scheme predicts a stopping cross section proportional to velocity  $v$ . In the Born approximation, there is an approximate threshold for  $\epsilon \sim 4$ . For a hydrogen projectile and for an ionisation potential  $I$  of the order of a few eV, the effective threshold would be about 100 eV, i.e. in a regime in which the experiment is very hard. This experimental difficulty is one reason why band gap effects are hard to find. Thirdly, an effective ionisation potential can be deduced by using the expression for the oscillator strength. This gives both a reasonable threshold and very good shell corrections.

The main conclusions from this work are that standard approximations work well for all but the lowest projectile energies, and that when there is a finite excitation energy, simple models suggest a bandgap threshold should be present.

#### 2.6. Role of the band gap

The main topic of this paper is the effect on collision cascades of ion-to-electron energy transfer. Such transfer clearly depends on the electronic excitations themselves. The simplest classification of such excitations is whether or not there is an energy gap, so it is necessary to look again at the long-standing question of whether or not the gap should have an effect on observed behaviour.

For metals, there are electronic excitations which require negligible energy. This is why their electronic conductivity is relatively high at low temperatures, and why the thermal conductivity is high too, though one must remember that diamond has a higher thermal conductivity than copper over a wide range of conditions. Thermal conduction is surely important in recovery from cascades, and we return to this in section 4.

The gap is also important in determining how many carriers (electrons and holes) are produced when energy is supplied. Charge production influenced the extent to which electric fields build up in irradiated solids, these turn affecting subsequent thermal steps. Such fields have been used as a possible basis for track formation, for discharges and for some of the differences seen in sputtering between insulators and metals [17]. It is helpful to note that there is a characteristic relaxation time for fields in a material with a dielectric constant  $\epsilon$  and electrical conductivity  $\sigma$ . The relation [18] is given by

$$1/\tau = 4\pi\sigma/\epsilon \approx 10^{13}\sigma[\Omega^{-1}\text{s}^{-1}]/\epsilon[\text{s}^{-1}].$$

The time is thus of order  $10^{-5}$  ps for a good metal, 1 ps for a very poor metal, and 1000 s for a good insulator.

To the best of my knowledge there is no unambiguous evidence that the clear threshold corresponding to the band gap actually shows up in the stopping of ions. Why not, for the models of section 2.5, suggest there should be a threshold? I can only propose that, as a rule, ions generate carriers (valence band holes and conduction band electrons) whose scatter does not have a threshold and so masks any effects. This is a feature missing in any harmonic oscillator model, where electrons remain bound (effectively there is an infinite confining potential) and with a minimum excitation energy of the oscillator energy for any level of excitation.

### 3. Solid-state phenomena

Before turning to the main topic of this paper in section 4, it is useful to note some related phenomena in nonmetals. These concern principally the distinction between the complex sequence of processes which occurs on a short time scale and the measurable consequences after these have settled down, and the cases where energy transferred from ions to electrons leads to structural changes which then affect the response to subsequent ions.

#### 3.1. Transient versus permanent damage

In most studies of irradiation damage, the defects observed are examined long after the event; indeed, the specimen may have been thinned, or subject to a range of cleaning and annealing steps. The defect populations measured are therefore not those created initially.

For insulators, a range of spectroscopic tools shows how the defects evolve, even on a very short time scale. In an alkali halide, for instance, the sequence following mere optical excitation would include those processes [19]:

- (1) generation of an exciton;
- (2) exciton self-trapping;
- (3) nonradiative transition from an excited state to generate a close neutral halogen vacancy and interstitial pair;
- (4) separation of the vacancy–interstitial pair through a focussed collision sequence along a close-packed halogen ion row.

These processes (taking nanoseconds only) are followed by various aggregation processes, depending on temperature and dose. Interstitials aggregate in various ways, leading to loops; how perfect interstitial loops are formed from initial damage on only one sublattice is interesting for various reasons. Vacancies aggregate to give colloids, which may, in turn, evaporate at higher

temperatures to produce other defect structures. Not all these processes occur in the metallic targets common in atomic collision studies, yet many of these processes have parallels which will be noted in section 4.

The point of examining insulator behaviour is that the wealth of information can be used for ideas about behaviour in metals. Here, low-temperature self-ion irradiation generates a cascade, often regarded as quasi-molten (indeed this is in line with molecular dynamics studies). Interstitials tend to move out and are retained by sinks; as “solidification” proceeds from the outside, vacancies (possibly swept in; there are analogies with laser annealing which could be exploited) aggregate to form loops. But the process is not simple, nor is it clear how to interpret an observed yield.

#### 3.2. Thermal versus high-energy processes

Here some of the secondary consequences of atomic collisions are noted, since these can obscure the link between the key processes and the observed outcome. If we propose energy is given to electrons by the hot ions in a cascade, we may ask what happens to that energy. Observation suggests that in insulators it causes photochemical processes producing defects, in semiconductors it leads to recombination-enhanced diffusion; in metals, observation is ambiguous.

In all cases, however, we may distinguish between fast particles, with energies well above  $kT_B$  ( $T_B$  is the bulk solid temperature) and the thermal processes, like diffusion, which follow. Thus, electrons may be re-distributed by (effectively) thermionic motion from a hot region and trapping outside; the electric fields they set up may bias diffusion processes. The main interest in the present paper lies in the rapid transfer of energy from ions to electrons (largely “high-energy processes” in the present context) whereas in most cases we shall see the consequences of a mixture of the several classes of higher energy and thermal processes (fig. 1).

#### 3.3. Structural matters

The amorphisation of crystalline solids can occur by mechanisms which may be purely ionic (i.e. ones which would occur in billiard-ball models) or which may involve a significant electronic component. Amorphisation clearly affects special features of ion-beam interactions in solids – like channelling – and so that any ion–electron energy transfer could have measurable consequences through this route. An issue here concerns the various forms of “amorphous” oxides and the ways in which they might be created. The common glasses, for instance, comprise network modifiers (alkalis like Na) as well as network formers, like Si or B, or Ge or P. Yet there are many other systems which form glassy states, such as  $As_2Se_3$ , or  $BeF_2$ , or  $ZnCl_2$ . By special

processing, especially rapid solidification, a much wider range of oxides form glasses (e.g. the oxides of Te, Mo, W and V) and the distinction between modifier and former is less clear. One way of looking at ion-beam amorphisation might be to suggest there is local melting and rapid solidification, but that is simplistic. The amorphous state formed under heavy-ion irradiation may be different again, at least partly because it will form in disordered regions which are constrained by a crystalline matrix, at least initially, prior to the overlap of such damaged regions. The metastable state, where crystal habit survives but internal anisotropy is lost, indicates the range of ways disorder can be achieved.

The amorphous state is a simple example of a structural change in which a chemistry-dependent phenomenon (i.e. electron-state-dependent) can influence an ionic radiation response, like nuclear displacement. Further, the amorphous state is metastable, and the degree of amorphisation or of recrystallisation may tell us something about the period for which a “melt” existed in a cascade. It could therefore be instructive to make measurements on glassy systems at a range of target temperatures, not only on defect populations of crystalline metals.

#### 4. Electron–nuclear energy exchange and modelling

##### 4.1. Equilibration and hot spots

The qualitative picture of the highly excited centre of a cascade has been common for many years. The demonstration of this behaviour in computer simulations has verified many of the intuitive ideas. Yet doubts remain about whether this picture is sufficient. On the one hand, some materials which appear very similar (e.g. Cu and Ni) actually behave somewhat differently [10]. Further, there is a feeling that the processes are

sufficiently fast that even electronic transitions may not equilibrate, and, if so, that the electrons may play a role as an energy sink or for energy transfer which goes beyond that as a component of the interatomic potential. The need for new ideas here has been stimulated by several pieces of work, notably the discussion of the equilibration process by Flynn and Averbach [20]. However, there were already many hints from other work, including laser annealing and transient behaviour in semiconductors.

*Equipartition model.* It is helpful to begin by describing two simple cases. The first concerns equipartition of energy in a cascade. Suppose there are  $N$  atoms within a “cascade zone” (a term which is loose in meaning, but not critically so) and suppose that there are  $Z$  valence (conduction electrons plus others readily excited) associated with each atom. If there is a total energy  $\epsilon$  injected by a projectile,  $N$  particles would gain energy described by a temperature rise of order  $E/Nk$ ; however, if the electrons constitute independent particles and equilibrium is achieved, the temperature rise would be lower, only of order  $E/(1+Z)Nk$ , with the electron and nuclear motions temperatures. The temperature lowering would, of course, affect time scales and thermal processes as de-excitation proceeded. Neglect of electron phonon coupling might lead to major overestimates of thermal spike temperatures: if  $\theta_0 = 10$  eV/ion and if  $Z = 10$ , then the electron temperature will remain well below the Fermi temperature.

*Thermodynamic model.* The second simple case takes this picture one stage further (fig. 2). We assume that we may regard the solid as three component systems, and that each can be characterised by a temperature; we now look at energy exchange between these components. Such a model has been used previously for the so-called phonon bottleneck problem in spin–lattice relaxation [21], and it provides a useful, if simplistic, framework. The three systems here are

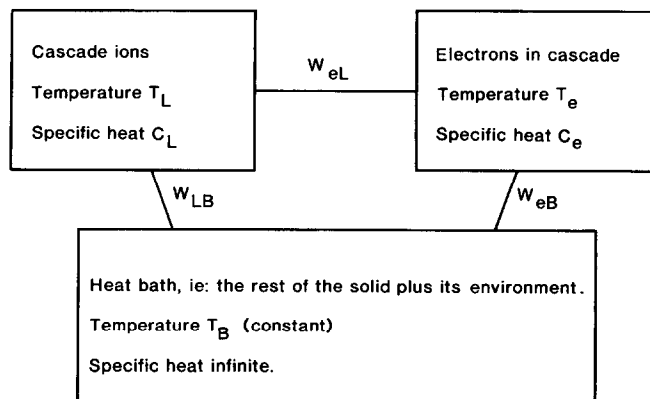


Fig. 2. Thermodynamic model for energy transfer in cascades. Note that the existence of a temperature for each component is presumed.

- (1) The cascade nuclei (plus core electrons moving rigidly with them), which have temperature  $T_L$  and specific heat (total)  $c_L$ .
- (2) The electrons which are dynamically independent in the cascade zone, and which have temperature  $T_e$  and specific heat  $c_e$ .
- (3) The rest of the solid, which stays at a constant ambient temperature  $T_B$  and, like all ideal heat baths, has infinite specific heat.

We may now ask what rate of equilibration is to be found in different circumstances for various possible energy constants  $W_{ij}$ . This is most easily done by writing down the energy transfer equations for the three systems; in these we may assume the rates depend linearly on temperature differences, though the transfer coefficients will depend on the actual temperatures.

If there is no electron phonon coupling (i.e. no energy transfer between systems (1) and (2), though each interacts with the heat bath) then:

- (a) the hot ion temperature decays with a characteristic time constant

$$\tau_L^{-1} = W_{LB}/c_L;$$

- (b) the electron temperature recovers with time constant

$$\tau_e^{-1} = W_{eB}/c_e.$$

$W_{eB}$  will usually exceed  $W_{LB}$  because electrons dominate heat conduction in metals. These rates are both ratios of heat transfer coefficients  $W$  to specific heats. When there is energy transfer between the two cascade subsystems, we shall need the ratio of the specific heats (it is effectively this which appears in the equipartition argument above), and we define  $\sigma = (\text{nuclear specific heat } c_L)/(\text{electronic specific heat } c_e)$ . This ratio is large because  $c_e$  is small for  $T_e$  much less than the Fermi temperature.

For very rapid transfer of energy between these two subsystems, the time  $\tau$  characterising their common trend to ambient temperature is

$$\tau^{-1} = (\tau_e^{-1} + \sigma\tau_L^{-1})/(1 + \sigma),$$

with obvious limits depending on the relative sizes of the terms. For a Fermi gas of free electrons,  $c_e$  is very small ( $\sigma$  large) and the characteristic time  $\tau$  is essentially  $\tau_L$ ; if transfer is rapid, the simple models apply.

Another ratio of importance concerns how fast equilibration is between the L and e systems, relative to the rate at which these combined systems (fast-electron–nuclear equilibrium) equilibrate with the heat bath. The ratio is:

$$\frac{\text{Equilibration } (\tau_{eL}^{-1})}{\text{Mutual recovery } (\tau^{-1})} = [W_{eL}/(W_{eB} + W_{LB})] \left[ (1 + \sigma)^2 / \sigma \right];$$

so, when one of the specific heats is much larger than the other ( $\sigma$  large or  $\sigma$  small) the equilibration between electrons and ions is much faster than their joint recovery. This is fairly obvious, of course, since the system with the smaller capacity rapidly adopts the temperature of the other, and the large heat capacity determines the sluggish return to the bath temperature. The model shows that there are two possible regimes: *electronic heat conduction* dominant and the *electronic heat sink* dominant.

*Molecular dynamics with electronic damping.* One way to model the effect of an electronic heat sink is to include damping within molecular dynamics. Suppose an ion of energy  $E$  enters the solid with mass  $M$  and velocity  $V$  so that  $\frac{1}{2}MV^2 = E$ . The rate of electronic energy loss is then  $AV$  (cf. section 2) at least for lower velocities. If, by collisions, this energy were shared over  $N$  ions, we find the electronic losses *increase*. For equal sharing, each of the  $N$  ions has  $E/N$  energy, i.e. velocity  $v = V/N^{1/2}$ ; each has an electronic loss  $Av$ , so that the total loss to the electrons is  $NAv = AVN^{1/2}$ . Redistribution of energy matters because the kinetic energy and friction depend on the ion velocity in different ways.

This is evident in the calculations of Jakas and Harrison [22], who looked at cases where losses were only by the incident ion, only by cascade ions, and other combinations. They found much bigger effects whenever damping of the large number of cascade ions was included, in line with the simpler arguments just given.

#### 4.2. The Flynn and Averbach model

What Flynn and Averbach did was to examine some of the issues just raised within a solid-state model. There are, of course, simplifications still, but some of the features are new, notably in their rough estimates of the rates  $W$ . They make four main observations. First, one characteristic length of importance is the electron mean free path in a metal. This mean free path falls as the temperature rises. It does so because of the enhanced scattering as the characteristic displacements of ions from their perfect crystal sites rise. At low temperatures one uses the description “phonon scatter”, but the phenomenon is more general, and better described by saying that there are both elastic scatter and energy exchange with lattice vibrations. Roughly, the mean free path  $\lambda = A/T$  is inversely proportional to temperature (here  $T$  would be  $T_L$  in the cascade and  $T_B$  outside it). Such mean free paths can also be estimated from resistivity data for liquid metals. Secondly, if the kinetic energy of  $N$  atoms in a region of radius  $r$  is raised to temperature  $T$ , then the total energy input is  $Q = NkT$ ; for a given  $Q$  and  $T$ , the radius containing  $N$  atoms is then  $r = B/T^{1/3}$ . Again,  $T$  means  $T_L$ ; note that  $r$

(hence  $N$ ) is assumed but will be determined by the points discussed in section 2.2. The third point concerns the ratio of the two lengths. It is found that situations can occur when the electron mean free path is much longer than the hot zone radius (low  $T$ ) or much shorter (high  $T$ ). These two cases correspond to quite different equilibration conditions. It is here that the fourth point arises. If one asks whether the electrons and ions can equilibrate ( $T_e = T_L$  in my nomenclature) then this proves possible only for radii  $r$  less than some critical value  $r_c$ .

The important point is that here the lattice is heated first (by nuclear collisions) and the electronic heating follows after energy exchange, and then only to a limited degree. The issue Flynn and Averbach raise is whether an individual electron, diffusing in the cascade with mean free path  $\lambda$ , will pick up enough energy in collisions within the cascade to reach the temperature which characterises the ionic motion. The question we must address is whether this matters for the ionic motion as monitored by defect yield, for the electronic excitation itself is not observed directly.

*Landau's transport equation for plasmas.* In 1936 Landau [23] derived a transport equation for particles of various types interacting by Coulomb forces. One result concerns the evolution of the electron temperature  $T_e$  towards the ion temperature  $T_L$ :

$$dT_e/dt = -(T_e - T_L)/\tau(T_e).$$

The expression for  $\tau$  can be rewritten in terms of the electron plasma frequency  $\omega_p \equiv [4\pi N_e e^2/m_e]^{1/2}$ , the screening length  $l_D \equiv [kT_e/4\pi e^2]^{1/2}$  and a length  $l$  characterising electron spacings,  $N_e l^3 = 1$ . If  $N_e = N_i$  (i.e. one electron per ion)

$$1/\tau = A(m_e/M_i)f(l/l_D)\omega_p,$$

where  $A$  and the function  $f$  will not be needed in detail here. Typically  $1/\tau$  is slower than  $\omega_p$  by 6–7 orders of magnitude, i.e. the nanosecond time scale. Landau's expression is not the same as that of Flynn and Averbach, which is based on a simple collision-rate argument. The mass factor means that the electron and ion subsystems equilibrate separately faster than they exchange energy, partly justifying the assumptions of well-defined ion and electron temperatures in the thermodynamic model.

#### 4.3. Energy transfer and energy sinks

Whether or not the ionic motion depends on the electrons in metals depends on the effectiveness of the electrons as an energy sink, their effectiveness in the conduction of heat, and the extent to which the electrons can cause other behaviour. We can recognise from simple solid-state arguments that (a) on the whole electrons are a poor energy sink, with a very low specific

Table 1  
Comparison of parameters for Cu and Ni

System	Specific heat [total, kcal/mol]	Thermal conductivity [total, W/cm deg]	Plasmon energy [eV]
Copper	120	4.26	15.2
Nickel	152	1.06	19.4

heat so long as Fermi statistics apply; (b) that on the whole electrons are a very good means of transferring heat: the thermal conductivity of almost all metals (including transition metals) is dominated by the electronic part, as shown by the respectable validity of the Lorentz and Wiedemann–Franz rules, and (c) that the extent to which defect processes occur in a transiently damaged region depend strongly on the temperature versus time behaviour.

In the Flynn–Averbach picture, when the electron mean free path is comparable with the radius of the cascade zone, the electrons are not heated to equilibrate with the ions in their passage through the zone. Yet the electrons may still carry away substantial amounts of energy, thus redistributing energy on the scale of their mean free path. This can be made quantitative by generalising the thermodynamic model of section 4.1 by replacing the simple transfer coefficients for energy to the bath by the relevant parts of the heat conduction equation [24].

There is therefore a group of parameters which we may wish to compare when contrasting different possible behaviours. As representative systems, we might look at Cu and Ni (see table 1). Note first that the specific heats at higher temperatures should be fairly constant (the Dulong Petit law) when expressed per atom, so that differences in the first column relate to density. Secondly, there is no electronic contribution to the thermal transport in nonmetals (though clearly thermally excited electrons can contribute) so insulators will usually have low  $k$ . Thirdly, the plasmon energy depends mainly on valence electron density, and hence on the number of electrons per atom (alkalis have low energies) and on atomic densities. Fourthly, returning to the specific and to the electronic thermal conductivity, a critical factor is the nature of the conduct ion electrons. For Cu, the Fermi energy lies in the relatively diffuse 4s band, with a low density of states at the Fermi energy; for Ni it lies in the narrow band of 3d states, where there is a much higher density of states. This is the main source of differences between Cu and Ni, and we can see how we might identify other systems as ones for which Cu is typical, or vice versa.

The simple picture to emerge is that if electrons provide *energy transport*, Cu does this most efficiently; if electrons act as an *energy sink* then Ni is the most effective.



#### 4.4. Other excitations

The discussion of electronic contributions so far concentrates solely on single-particle excitations. Yet there are also the collective excitations, the plasma oscillations of the electron gas. The energies of plasmons are typically 10–30 eV for metals, so that the excitation can act as a sink for a significant energy. Values are often similar for valence electrons in non-metals, where, of course, the one-particle energies have a threshold corresponding to the band gap.

The plasmon excitation is not simply a sink of energy, for the plasmons can decay in various ways. These have been reviewed in the context of laser annealing [25]: the plasmons decay with little transfer of energy to the lattice, mainly exciting individual electrons. In many cases of interest to us the plasmons will be too large in energy to be too important. Yet there are special cases for which they are of interest. For instance, photodesorption from small alkali metal clusters has been observed following excitation of surface plasmons by low-intensity light [26]. This – for a metallic system – is the analogue of some of the photochemical processes observed in nonmetals [19,27].

#### 4.5. Observations on cascade collapse in Cu and Ni

One striking observation concerns the vacancy loops left after a cascade. Various studies (for example relating to alloy disorder) verify a picture which suggests that, in a cascade, one may imagine an initial period loosely akin to a molten state, followed by solidification from the outside inwards. Point defects created have different fates: interstitials tend to be mobile enough to reach sinks, like surfaces or grain boundaries. Vacancies appear to be pushed ahead of the solidification front. Why this happens is a separate matter; there are analogies with the dynamic segregation observed in the solidification during laser annealing, and there are much simpler aspects like the higher equilibrium numbers of point defects in hotter regions. The key is that the vacancies can form dislocation loops, and so give an observable reminder of their (transient) existence. One can go further, however, and check how complete the loop formation was. If, after an initial low-temperature irradiation, one checks the numbers of loops, and then raises the temperature, are still more loops seen? If yes, the completeness of the thermal processes was not achieved at the lower temperature; presumably the cascade cooled too fast.

English and Jenkins [10] looked at the data systematically for a number of metals, noting various cautions as regards other phenomena like loop shrinkage, etc. They use two main parameters to characterise the results. The first is  $Y$ , the defect yield:

$$Y = \frac{[\text{vacancy loop concentration}]}{[\text{number of cascades/unit vol., energy above } E_t]}$$

and  $\epsilon$ , the cascade efficiency:

$$\epsilon = \frac{[\text{number of vacancies in loop-form}]}{[\text{number of vacancies predicted in cascade}]}$$

Some of the results come from structural features:  $\epsilon$  and  $Y$  are higher for fcc metals and lower for bcc or hexagonal metals. Other features relate to energetics, in that  $Y$  tends to be higher for lower stacking fault energies. Does transfer of energy to and by the electrons affect the completeness of the process of cascade collapse?

The observed yields are noticeably different for self-ion irradiation:

Cu/30 keV Cu <sup>+</sup>	0.5 ± 0.01,
Cu/90 keV Cu <sup>+</sup>	1.1 ± 0.1,
Ni/50 keV Ni <sup>+</sup>	0.2,
Ni/100 keV Ni <sup>+</sup>	0.1,

with those for Ni being low. Can we explain this with electron–phonon interactions? Qualitatively, it seems that Cu has a higher yield because Ni quenched so rapidly that loops could not form. Quantitatively, this remains to be demonstrated, though the conclusion is in line with other data on the anomalous reduction of Stage I recovery in Ni after heavy-ion irradiation [28].

## 5. Conclusions

Ion/electron energy exchange is undoubtedly important in nonmetals: in insulators for defect production, and in semiconductors for defect motion. In metals, the likely role is energy transport and as an energy sink, but the importance is far from settled. Modelling these systems properly will be hard, both because of the degree of electronic excitation and because the Born–Oppenheimer approximation may well fail. Yet there is plausible evidence in favour of this energy exchange, and future experiments should establish the extent of the phenomenon more precisely.

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