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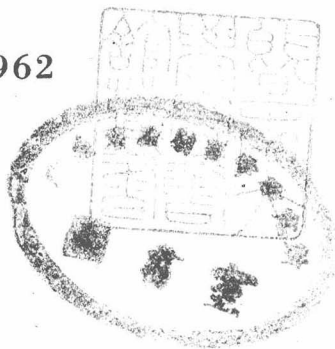
a cura di D. S. BILLINGTON
Direttore del Corso

CENTRO DI STUDI NUCLEARI DI ISPRA
DEL COMITATO NAZIONALE PER L'ENERGIA NUCLEARE
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Radiation damage nei solidi

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Introduction.

D. S. BILLINGTON

Director, Solid State Division, Oak Ridge National Laboratory ()
Oak Ridge, Tenn.*

Nature has, through the agency of radioactive impurities in crystalline solids, presented us with evidence, the metamict minerals, that radiation damage is indeed an old subject. However, for man, the subject has received its principal impetus from technological requirements generated by the nuclear reactor developmental programs; and as such radiation damage is definitely established as a major area of concern in the reactor field. This aspect of radiation damage is important, challenging, and of utmost concern to ourselves and future generations in our quest for the cheap and plentiful power that all nations require for a modern technology.

On the other hand, that which begins as a problem of engineering concern is rapidly becoming a most important tool for the study of the behavior of solids. Almost coincidental with the beginnings of nuclear reactor studies has been the realization by solid state physicists of the crucial role that lattice defects play in determining so many important properties of a solid. For example, the concept of dislocations and the subsequent experimental verification of the role of dislocations in explaining the plastic properties of solids is a major example of the role of lattice defects in determining solid state behavior. The role of Schottky defects in explaining diffusion and related reactions in solids is of equal importance.

Radiation damage studies assume the aspect of a tool for solid state investigation because the interaction of energetic radiation with solids leads to the introduction of lattice defects into the solid. Thus, energetic radiation becomes a tool for manipulating a solid, in ways that are both unconventional and unique. For example, many solid state reactions will take place at lower temperatures, after or during irradiation, than in the absence of radiation.

(*) Oak Ridge National Laboratory is operated by the Union Carbide Corporation for the U.S. Atomic Energy Commission.

Crystals can be hardened by irradiation, but in a manner that is unlike either cold-working or alloying. They can be heat treated without resorting to heat. Under special conditions, transient defects can be introduced, such as the thermal spike. Phase changes can be made to take place under abnormal conditions. High-temperature phases can be made stable at room temperature by irradiation alone.

Thus, irradiation of solids by energetic radiation can lead to changes in the solid that are often similar to effects generated by other defects, but in the last analysis there remain many unique aspects.

However, we do not understand in detail the mechanism of the interaction of energetic radiation with the crystalline structure. This is partly caused by the fact that we do not have a detailed understanding of lattice defects in the absence of radiation. On the other hand, it is safe to say that we probably won't understand defects in the absence of radiation until we understand in detail the radiation damage process. This is to say that radiation damage is integrally bound up as an inseparable part of the whole field of solid state physics, and to understand the part we must understand the whole. It is my belief that the increased interaction or cross-fertilization that is taking place between the two fields of endeavor is desirable and necessary to gain ultimate understanding of solid state behavior.

In arranging the present series of lectures and seminars, it was considered important that several series of lectures should be presented: First, a series of lectures on defect solid state in the absence of radiation. Second, a thorough discussion of radiation damage theory with emphasis on the basic mechanism of interaction of radiation with matter. Third, an authoritative discussion of recent advances in the experimental observation of lattice defects. Fourth, detailed discussions of recent advances in radiation damage studies on all types of solids—metals and alloys, semiconductors, ionic and covalent crystals. Fifth, seminars on recent advances in all the above four categories.

It is my belief that the lectures and seminars that were given presented an excellent cross-section of the entire field of radiation damage in solids and should lead to an informed viewpoint of the many problems in the field that remain.

It is known that the many speakers who graciously consented to give these lectures and seminars represent an appreciable fraction of the outstanding workers in the field in the world today. Participation in the School has provided a unique opportunity, not only to the «students» but to the faculty as well, and has proven, I'm certain, to be of inestimable value to each and every one of us.

The devoted attention and skill applied to the problems of managing the School by Dr. A. MERLINI, the Scientific Secretary, and his staff, are deeply appreciated. The gratitude of all is expressed for the hospitality and co-oper-

ation of CNEN and EURATOM. The assistance of Mrs. A. MERLINI, given under trying circumstances, is most appreciated. Professor POLVANI and Professor GERMANÀ, with their usual foresight and thoughtfulness, provided the congenial and challenging environment that enabled this School to meet the high traditions set by the past Summer Schools sponsored by the Italian Physical Society.

Crystalline Defects and Their Detection.

Introductory Lectures on Crystalline Defects.

J. FRIEDEL

Physique des Solides, Faculté des Sciences de Paris, Orsay

Introduction.

The purpose of these introductory lectures is to remind you of the main technical terms about defects in crystals which will be used in the study of radiation damage. Defects in crystals arise, of course, either from deviations of the nuclei from their periodic arrangement, or from excitation of electrons from their most stable state around the nuclei. There are many types of such defects, most of them of importance in radiation damage. But, very roughly speaking, one can distinguish the dynamic ones, which only last as long as some external excitation or little time afterwards; and the static ones, which remain, in a metastable state, long after the external excitation has ceased. Because time is short, I want to concentrate on the static defects. But to be complete, I shall first summarily list the dynamic ones of importance in radiation damage.

I. - Dynamic Defects.

1. - Electronic excitations.

These are of fundamental importance in the slowing-down of charged particles.

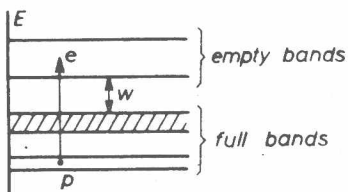


Fig. 1. - Individual electronic excitation.

Those of major importance can be thought of as excitations of *individual electrons*: in the band approximation, one electron e from a full band is excited into an empty band of higher energy E , leaving a positive hole p behind [1] (Fig. 1).

The recent studies of electronic correlations [2] have essentially confirmed this simple picture. The Coulomb interactions between the electrons e and

the incoming charge Ze are merely screened off [3], so that their potential energy of interaction V is cut off in a roughly exponential way with distance r :

$$(1.1) \quad V \simeq -\frac{Ze^2}{r} \exp\left(-\frac{r}{r_0}\right).$$

For incoming charges moving slowly with respect to the electrons of the material, the screening radius r_0 is given approximately by a Debye formula,

$$(1.2) \quad r_0 \simeq \frac{v_M}{\omega},$$

where v_M and ω are a characteristic velocity and a characteristic frequency associated with the electron gas. More precisely, ω is the « plasma » frequency:

$$(1.3) \quad \omega \simeq \left(\frac{4\pi N e^2}{m} \right)^{\frac{1}{2}},$$

where e and m are the charge and mass of an electron, and N their density in the material. v_M is a characteristic velocity, which, for a metal, would be the Fermi velocity. For particles with higher velocities, the screening radius increases [4]. Roughly speaking, the effective ionization of the particle increases, in a way which justifies Bohr's approximate condition [5] about the particle velocity compared with the electronic velocity.

Electronic correlations now replace the long range Coulomb interactions by the « plasma » waves [8], that is longitudinal collective excitations corresponding to successive excess and lack of electronic density, as pictured in Fig. 2. Experiments on many materials have shown that such waves exist [7], with frequencies approximately given

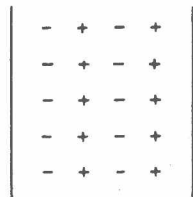


Fig. 2. Plasma wave.

by eq. (1.3): one shoots fast electrons through thin foils and measures their energy losses, which are multiples of the plasma energy $\hbar\omega$. In formula (1.3), one must count only the easily polarizable electrons, thus those with an excitation energy w , Fig. 1, not too large compared with the plasma energy. In most materials, all the valence electrons fulfil this condition [8]. It seems, however, that the excitation of plasma waves is not very important compared with individual excitations, except in the slowing-down of fairly slow charges [3].

The *excitons* are another type of excitation made possible, in insulators, by electronic correlations: they occur when the excitation energy ΔE given to the electron is too small ($\Delta E < w$, Fig. 1) so that the electron is kept

bound to the positive hole and forms a neutral defect [9]. This type of defect has also been very much studied in recent times [10], but is probably often of not much importance in the slowing-down processes.

2. - Photons.

These are, of course, significant both as producing radiation damage (γ -rays) and as light or X-rays emitted as result of radiation.

3. - Displacement of nuclei.

These can sometimes be analysed in terms of *phonons*, that is plane waves of atomic displacements small enough to be treated within linear elasticity. This is especially true for the general displacements produced some way from the initial displacement hits. The movements of the atoms might even be disordered enough for the concept of temperature to be used, *i.e.*, the equipartition of energy between the various phonon modes [1]. The dispersion curves of the phonons, *i.e.*, the variation of their frequency with wavelength, are also important in telling us something about the interatomic



Fig. 3. - Crowdion along a row AB .

forces in the crystals. This is why these curves are so much studied nowadays by X-rays or neutron scattering [12]. It is however clear that a knowledge of phonons alone is quite insufficient to discover the nature and the value of the interatomic forces involved in the very large displacements occurring during radiation damage. The higher-order terms in elasticity (anharmonic terms) are of little use, if not pushed to very high orders indeed. One has had, therefore, to rely, in this field, up till

now, on very rough theoretical estimates or on indirect evidence about surfaces, grain-boundaries and liquids.

We can finally list two other dynamic defects, which will be discussed at length later on at this meeting. The *focussons* [13] correspond to the possibility for kinetic energy to be transmitted not through a volume, as in a phonon, but along a close-packed row in the crystal. It would indeed be difficult to describe such a progression in terms of phonons. The *dynamic crowdions* [14] correspond to a possible transport of matter along some rows in some crystal-line structures; the atoms along row AB , Fig. 3, push themselves in such a way that an excess atom progresses along the row.

II. - Static Defects.

These can be classified as follows, from a geometrical point of view:

1) *Point defects*: impurity atoms, either inserted into interstitial positions in the crystal, or substituted to atoms of the pure crystal. Vacancies are a particular case of the latter, where atoms are merely removed from lattice sites.

2) *Linear defects*: dislocation lines.

3) *Surface defects*: the outer surface of a crystalline sample is, of course, a break in the periodicity of the lattice; grain boundaries, between crystals of different orientation or chemical structures, are another example.

4) *Volume defects*: aggregates of various kinds, such as displacement spikes in radiation damage, Guinier-Preston zones in solid solutions.

Surface defects will be treated first, then dislocations and finally point defects.

1. - Surface defects.

1.1. *Outer surfaces*. - This type of defect, which separates the crystal from vacuum or from an atmosphere, is characterized by its surface tension.

a) The *surface tension* γ , can be taken as the excess free energy per unit area of the surface. It has been measured for instance by heating wires of various lengths, suspended by their ends, at a temperature high enough for creep to occur [15]. One then observes the larger wires to lengthen under their own weight; the shorter ones contract, under their surface tension (Fig. 4). The measurement of the intermediary length where the weight equilibrates the surface tension gives the latter quantity. One finds values of the order of

$$(1.1) \quad \gamma, \simeq \mu b / 10 ,$$

where μ is the elastic shear modulus and b the inter-atomic distance.

Such a value can be understood from the fact

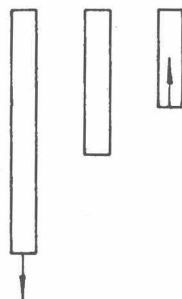


Fig. 4. - Measurement of surface tension.

that γ_s is the work done to break in two a crystal over a unit area. Let $\sigma(x)$ be the tension exerted to displace by x the two halves of the crystal with respect to each other (Fig. 5). For very small x , i.e. in the elastic range, σ must be of the order of Ex/b , where E is Young's elastic modulus. One also expects σ to vanish when x is large enough, because interatomic forces are only fairly close range. $\sigma(x)$ must therefore have a form such as that pictured in Fig. 6; and

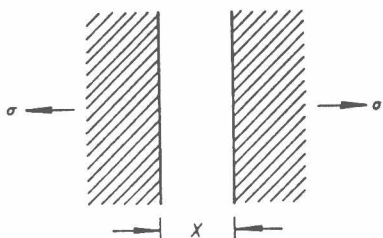


Fig. 5. — Tension to separate by x the two halves of a crystal.

$$2\gamma_s = \int \sigma dx.$$

A value near to (1.1) is obtained if $\sigma(x)$ is taken as a sinusoidal curve and vanishes for $x \simeq b/2$. Values of the order of (1.1) have also been obtained in a few cases where more detailed computations have been made. These involve a knowledge of the electronic structure of the surface.

b) The electronic structure of the surface differs, of course, depending on the nature of the material considered.

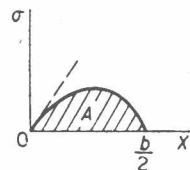


Fig. 6. — Variation of σ with x .

In *metals*, the surface tension is due to the valence electrons and arises from two quantum mechanical effects. If the potential V in the vacuum were infinite, so that the electrons were kept completely in the metal, their wave function ψ should vanish at the surface S (Fig. 7). This effect reduces

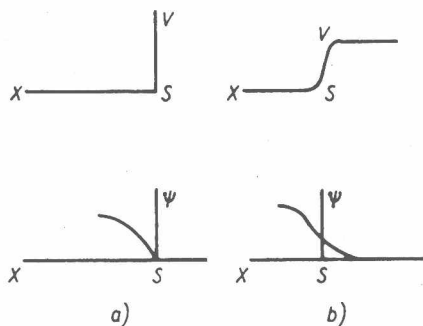


Fig. 7. — Behaviour of the electronic wave functions at the surface of a metal a) Impenetrable vacuum: b) real case.

tential higher than in the metal; energy [18].

their density near to the surface, thus increases their Fermi energy [16]. In actual fact, the increase of potential towards vacuum is more progressive and finite, as pictured in Fig. 7 b). As a result, the electron wave functions are able to penetrate a little into the vacuum, by a kind of tunnel effect, in such a way that the electronic charge in the vacuum compensates the lack of charge, near the surface, inside the metal [17]. But the electronic charge in the vacuum is submitted to a potential higher than in the metal; this effect also produces an increase in

In *covalent* structures, the surface tension is best computed by counting simply the number of bonds broken by the surface [19] (Fig. 8). Excess electrons can actually be captured on the surface to saturate these broken bonds. In other words, the surface gives rise to acceptor levels in the forbidden energy gap, which are usually fairly stable below the conduction band (Fig. 9). In an *n*-type semiconductor, these surface levels are thus filled at the expense of the shallow impurity levels, turning the surface layer into *p* character (Figs. 8 and 9). Such a layer is well established in materials such as germanium [20].

Finally, in *ionic solids* [21], the surface tension arises from the work done against the electrostatic forces to remove one half of the crystal (Fig. 10). The removal of the dashed half of the crystal, Fig. 10, disturbs the electrostatic balance; thus part of the positive charge of ion *A* is no longer compensated by the negative ion *B*. One can think that there are now uncompensated charges of alternate signs on the surface ions, and that the surface energy arises from their Coulomb interactions. A simple reasoning shows that, for structures with equal numbers of positive and negative ions of charges $\pm Ze$ the uncompensated charges are equal (*) to $\frac{1}{2}Ze$.

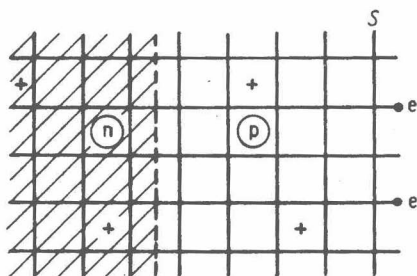


Fig. 8. — Broken bonds on the surface *S* of a covalent structure: *p* character due to captured electrons saturating some bonds.

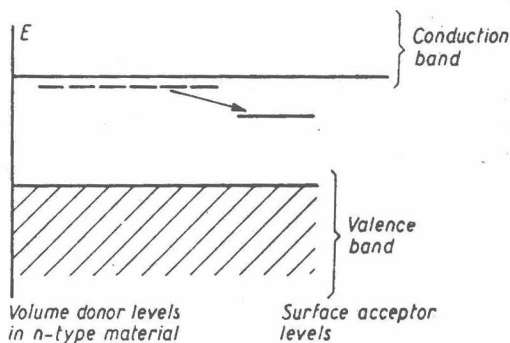


Fig. 9. — Saturation of surface acceptor levels by volume donor levels, giving rise to a *p* surface layer in an *n*-type semiconductor.

c) The surface tension is obviously *anisotropic*. In metallic or covalent structures, it is smallest for close packed planes; for covalent structures, more bonds are broken, obviously, for the atomically rough surface of Fig. 11 *b*) than for the smooth one, Fig. 11 *a*); in metals, electrons are more simply reflected by the latter than by the former, and this should correspond to a

(*) This is easily seen by thinking that the addition of the dashed plane of ions, Fig. 10, changes the signs of the uncompensated charges without altering their absolute magnitude.

more stable state. In ionic solids the uncompensated surface charges should cancel each other at close range: in Fig. 12, *a* is more stable than *b*.

Perhaps a physically more important problem is whether, for a given orientation, a roughness on an atomic scale is more or less stable than on a larger one (Fig. 11 *b* or Fig. 13). In

				S
-	+	-	+	--
+	-	+	-	\div
-	+	-	+	$\begin{matrix} A \\ B \end{matrix}$
+	-	+	-	--
				\div

Fig. 10. — Surface tension in ionic solids.

most cases this problem is not clearly settled either theoretically or experimentally. My personal feeling is that atomic roughness should be somewhat more stable in metals and covalent structures. This is because the electrons should be able to rearrange themselves more easily on isolated atomic steps than on larger ones, so that an atomic step should be more stable when isolated than when included in a larger one: covalent

bonds such as *b*, *b'*, Fig. 11, could stabilize each other; larger tunnel effects could occur on such steps in metals. Thus big steps should occur only in special cases: as configurations out of equilibrium, due to the kinetics of

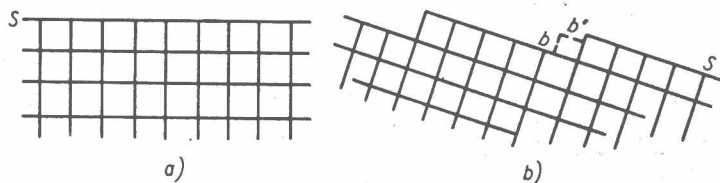


Fig. 11. — Atomically smooth and rough surfaces.

crystal growth or etching; or when there is an adsorbed layer of large atoms or molecules: these will obviously fit more easily to the big steps of Fig. 13. One expects the contrary to be generally true in ionic solids: each atomic step is obviously the site of an excess charge which is not necessarily compensated at very close range; in big steps between stable surfaces, of the type of Fig. 12*a*, only the corners such as *C*, Fig. 13, carry excess charges which are not compensated at close range. Observations on surfaces obtained by cleavage [22] or heated in various conditions [23] are, on the whole, in fair agreement with these conclusions.

S	—	—	—	—	—	—	S
+	-	+	-	+	-	+	+
-	+	-	+	-	+	-	-
+	-	+	-	+	-	+	+
						-	-

Fig. 12. — Two orientations of the surface in ionic solids.

d) As far as one can tell from the high-temperature measurements made so far, the surface tension seems to decrease somewhat with increasing temperature [15]. There is, therefore, a *positive surface entropy*.

The main part of it has probably a vibrational origin: the atoms on the surface can vibrate, normally to the surface, more easily than parallel to it or than atoms inside the crystal can do [24]. At temperatures definitely higher than the Debye temperature, the atoms can be assumed to vibrate independently from each other. The surface atoms have then one degree of freedom with a free energy:

$$F_s = kT \ln \frac{\theta_s}{T},$$

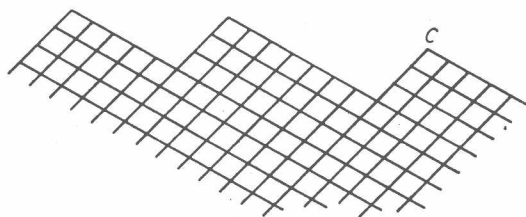


Fig. 13. - Microscopically rough surface.

which involves a Debye temperature θ_s somewhat smaller than the volume value θ_v . The corresponding excess entropy per unit area is

$$\Delta S_s \approx \frac{1}{b^2} \left(\frac{\partial F_v}{\partial T} - \frac{\partial F_s}{\partial T} \right) = \frac{k}{b^2} \ln \frac{\theta_v}{\theta_s} > 0.$$

Assuming that the elastic constant involved in θ_s is something like half that in θ_v , one finds for the entropy a reasonable order of magnitude.

There is also the possibility of a positional entropy: at finite temperature, one expects the steps on the surface to become covered with « kinks » (k , Fig. 14), and also adsorbed atoms and adsorbed vacancies to appear, if the crystal is in equilibrium with its vapour. All these defects are of course produced because of their entropy. However, as far as fairly rough theoretical studies indicate [25], this contribution should usually be negligible, except if surface melting occurs: above a critical temperature and by a co-operative process, the surface might become covered with kinked steps and adsorbed point defects. However, this critical temperature cannot be much lower than the (volume) melting point; and there is indeed no break in the decrease of γ_s with increasing temperature which might indicate that the process occurs when the crystal is in contact with its vapour. Indeed, surface melting seems to have been observed only for crystals in contact with their melt [26].

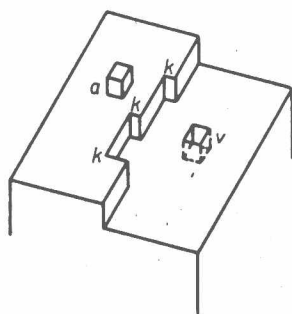


Fig. 14. - Surface at $T \neq 0^\circ\text{K}$, with kinks k , adsorbed atoms a and adsorbed vacancies v .

e) Finally, two points must be stressed in connection with *point defects*.

Surface diffusion is much more rapid than volume diffusion [27]. This is because volume diffusion occurs usually by vacancy migration. But vacancies