

goes from a normal to a superconductive state, and the electron distribution will be affected to some extent. Since the factors on which the lifetime depends change in the superconductive transition, it seems quite possible that the lifetime itself changes. Crude estimates indicate the lifetime might be lengthened.

2. It seems quite certain now^{1,4} that positronium formation plays an important role in the annihilation process. In fact the experimental data can be explained best by assuming that the positrons slow down rapidly, then form positronium, and finally annihilation takes place from the ground state of the positronium. The long-lived triplet state of positronium will be converted rapidly to the singlet state, by the interaction of the positronium with the lattice vibrations, or by collisions with other electrons. One of the typical features of the superconductive state is the inability of the electron system to exchange energy with the lattice system or with impurities. It has been recognized⁵ that in the superconductive state one has to deal with a wave function which is "adjusted" to the electron-lattice interaction, the electron-electron interaction and also to the interaction between the electron system and impurities. ("Adjusted" is used here in the sense that these interactions cannot cause transitions.) It seems quite possible therefore that the positronium exists in the system as some kind of impurity. In that case the interactions responsible for the conversion from the triplet to the singlet state would not operate, or would operate much less efficiently, in the superconductive state. Consequently the triplet state would persist longer in a superconductor than in a normal conductor. This would give rise to a complex lifetime decay of positrons in a superconductor. It is true that a second electron could in principle annihilate with the positron in the positronium; one finds, however, that when positronium formation itself is likely, this pick-off annihilation probability becomes quite small. Further, the average electron density around positronium is smaller than that around a positron, and this too reduces the efficiency of the "pick-off annihilations." (This type process was in fact invoked by Garwin⁴ to explain the long-lived component of the positron lifetime in some materials.)

3. Experiments done by Stump and Talley⁶ and independently by Millett⁷ indicate that the decay of positrons in lead at liquid nitrogen temperatures differs from that at liquid helium temperatures. The experiments at liquid nitrogen temperature yield the usual one-lifetime annihilation process (with the usual numerical value for metals), whereas those at liquid helium temperatures indicate a complex lifetime scheme with a longer-lived component.

4. On the basis of the model developed, one would expect more three-quantum annihilation processes in a superconductor since the triplet state has less chance to be converted. Experiments to check this feature are now in progress. If these same lifetime measurements were made at liquid helium temperatures in lead and if a magnetic field strong enough to destroy the superconductive state were applied, one should on the basis of previous considerations reobtain one-lifetime type annihilation. This last experiment would also decide whether the effects already observed are indeed characteristic of the superconductive state, or whether they represent some general property of metals at low temperatures.

Further details will be published in a more extensive communication.

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⁴ This point of view was expressed by Bohr in a discussion remark. [See *Physica* **19**, 762 (1953).]

⁵ R. L. Garwin, *Phys. Rev.* **91**, 1571 (1953).

⁶ The author is indebted to these authors for communicating their results before publication. These experiments will be reported at the Austin Meeting of the American Physical Society.

⁷ The author wants to express his gratitude to Dr. Millett for informing him about these results in advance of publication. These results, too, will be reported at the Austin Meeting.

Creation of Displacements in Radiation Damage*

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A THEORETICAL investigation has been started into the formation and character of the displacements created in face-centered cubic metals by radiation damage. (Displacements, or Frenkel defects, are caused when energetic particles drive atoms of the lattice to interstitial sites leaving vacancies in their original positions.) Attention has been concentrated here on low-energy collisions because most of the displacements are generally created by collisions with energies only a few times the threshold—in the range of one or two hundred electron volts. The procedure has been to consider that an atom at a lattice site, or in an interstitial position, receives a considerable amount of energy at a given instant and to attempt to determine the end state of the lattice as a function of the magnitude and direction of the original impulse. In this way the threshold energy for displacement creation can be calculated and presumably, for a given distribution of primary particle energies, the distribution in length of the resulting displacements, their spatial distribution, and their total number could be obtained.

It has been assumed that for close-packed metals at low energies the principal interaction between colliding atoms is the repulsion of closed shells, which may be approximated by a semiempirical formula of the Born-Mayer type, $V(r) = A \exp\{-(r-r_0)\rho/r_0\}$. The constants in the closed-shell repulsive potential depend to some extent on the assumptions used in determining them. It has been shown¹ that for copper the value for ρ can be bracketed between 13 and 17. Since this force law is very short-range, the procedure has been to predict the result of a particular collision on the basis of a billiard ball model where the size of the balls is determined by the interatom distance at the instant of contact, i.e., when the relative kinetic energy vanishes. At these low energies many-body collisions are important, and reasonable techniques have been evolved to treat such cases in a manner consistent with the rigid sphere model. So far only collisions have been considered where the high-energy particle moves in a crystallographic direction. The high degree of symmetry in these cases facilitates their treatment. From their study, one finds two close competitors for the mechanism of displacement creation with minimum energy.

For ρ equals 13 (for which the corresponding value of A is 0.053 ev), it is found that an atom at a lattice site needs about 18.5 ev to move in the (111) direction through the triangle formed by three of its nearest neighbors to the interstitial position. Comparable energy (17.5 ev) is required by a lattice atom moving in the (100) direction for displacement creation in a "knock-on" mechanism where the original fast atom moves to another lattice site displacing its neighbor to an interstitial position. The history of all these collisions is rather complex and we have had to resort to reasonable, though somewhat arbitrary, criteria for determining the thresholds. A further difficulty is introduced by uncertainty as to the equilibrium configuration of the interstitial atom.¹

Rough estimates have been made on the magnitude of these threshold energies on the basis of an alternate force law with $\rho = 17$ and $A = 0.038$ ev. They give 43 ev for the (111) mechanism and 34 ev for the knock-on collision. Experiments with electron radiation by Eggen and Laubenstein² report a threshold value of 25 ± 1 ev. Apparently this value lies well inside the rather wide limits set by the foregoing alternate calculations.

It was mentioned above that consideration was also being given to the history of energetic interstitial atoms. Such interstitials can be studied as typical atoms undergoing displacements longer than the minimum stable length. It appears that displacement length increases somewhat more rapidly than the logarithm of the energy.

Among the subjects planned for future study are (1) the replacement of the rigid body model by an improved treatment, and (2) the investigation of collisions undergone by atoms moving along directions of low symmetry. It appears that the rigid body

assumption may give rise to larger errors than were first anticipated. Information on collisions as a function of the general direction of the initial impulse is useful in establishing the displacement yield as a function of energy above threshold.

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Superconducting Compounds

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IN a previous paper¹ an outline was given of the necessary² though not always sufficient, conditions for the occurrence of superconductivity in compounds. Following the hypothesis of an optimum number of valence electrons per atom and of the increase of the transition temperature with an increase of volume, a variety of new superconducting binary and ternary systems have been found. They confirm the assumption that deviation from an essentially metallic bond is a necessity for superconductivity.

(a) *Phosphides*.—Until now, no superconducting phosphides have been known. Recently we have found that Mo₃P becomes superconducting near 7°K and Rh₅P₄ at 1.22°K. We are not quite certain yet whether these compositions correspond to a single phase and rely thus far on the reported crystallographic investigations.^{2,3}

X-ray patterns showed that in general we were unable to obtain these phases completely pure. In the case of Mo₃P, MoP was always present, and in Rh₅P₄ we always detected Rh₂P. Both MoP and Rh₂P, however, can be prepared without any other phases present and neither becomes superconducting above 1.03°K.

(b) *The NiAs Structure*.—As mentioned before,¹ several intermetallic compounds with this type structure have been reported as superconductors. However, no superconducting arsenides had previously been found. NiAs by itself does not show superconductivity above 1.28°K.^{4,5} Assuming now that the transition temperature, if present, could be raised by enlarging the crystal lattice (as pointed out before¹), we substituted the larger Pd partially for the Ni. This, however, cannot go all the way to PdAs, as this alloy is not isomorphous with NiAs, nor does PdAs become superconducting above 1.02°K. This attempt to enforce superconductivity was successful: the solid solutions from (Ni_{0.75}Pd_{0.25})As to (Ni_{0.12}Pd_{0.88})As become superconducting above 1.06°K. The maximum transition temperature is reached for (Ni_{0.25}Pd_{0.75})As at 1.6°K and decreases with either increasing or decreasing Pd amount.

(c) *The Rh-X System*. X=S, Se, Te.—From our previous considerations it had seemed likely that compounds of Rh with S, Se, or Te should also become superconducting.

We have found that Rh₃Se₈, which is a well-defined compound,⁶ becomes superconducting at 5.8°K.

According to Woehler⁷ and Biltz,⁸ the only compound in the Rh-Se system is supposed to be Rh₂Se₅. Now Rh₂Se₅ does not become superconducting above 1.04°K, whereas compounds with an approximate composition between 2Rh:3.4Se and 2Rh:4Se do become superconducting. In this Rh-Se system one does not seem to have a well-defined phase with respect to composition, as one does in the Rh₃S₈ case. The x-ray patterns indicate identical lattice structure for all those alloys whose composition lies between 2Rh:3.2Se and 2Rh:5Se. The lattice constant, however, rises as the Se content decreases. On both ends of the homogeneity range no superconductivity can be observed any longer above 1.02°K.

We seem to have here an example of the hypothesis according to which the transition temperature depends strongly upon the

volume and the number of valence electrons per atom.¹ Whereas an increase in Se decreases the volume and raises the number of electrons, an increase in Rh has the opposite effect, and one therefore seems to be able to cover the whole range in which superconductivity can occur. Consequently, the transition temperature rises and falls between 1°K and 6°K with varying selenium content. The optimum condition seems to be 2Rh:3.5Se with a transition temperature at ~6°K.

In the Rh-Te system the situation is similar but extends over a smaller range, as Te cannot replace Rh to the same amount as Se. The optimum condition is 2Rh:4Te, which becomes superconducting at 1.51°K.

It is our hope that more systematic measurements on the Rh-Se system will reveal the critical electronic condition for superconductivity in a given crystal lattice.

The x-ray identification and structure studies which Dr. S. Geller has made on these compounds have been most helpful. We are grateful to him for his interest and his assistance, and to Mr. A. N. Holden for valuable discussions.

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X-Ray Coloring of 400-Mev Proton-Irradiated KCl*

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THE total number of lattice defects produced by particle irradiation is an important quantity in the study of radiation effects in solids. In this connection, a possible correlation of the large decrease of density produced by 400-Mev protons in KCl with measurements of optical absorption is of interest since both effects may be interpreted in terms of a concentration of vacancies. An appreciable coloring of KCl crystals with the high-energy protons, however, is obtained in our experimental setup only at low intensity of irradiation ($mt = 1 \times 10^{15}$) which produces rather small changes in density. At intensities about five times higher, on the other hand, the density is altered considerably but the crystals are almost completely bleached, which is presumably because of a stronger heating of the crystals in the higher-intensity beam. In order to use this high-intensity irradiation, it appeared thus advisable to try to color the crystals with x-rays after they have been irradiated in a proton beam which is strong enough to produce large density changes. In a normal crystal, the coloring produced by x-rays falls off rapidly with distance attaining a value of $1/e$ at about 0.05 mm below the surface.¹ Thus, if the proton-irradiated crystals could be bodily colored by x-rays, then this would indicate that vacancies produced by protons can be subsequently filled by x-ray photoelectrons. It would provide also a further evidence for the basic role of the soft component of the x-ray radiation in producing color centers.

To test these ideas, crystals, which were essentially uncolored by proton irradiation in the Carnegie Institute of Technology cyclotron, were exposed to x-rays from a molybdenum target tube which had a beryllium window and was operated at 45 kv and 18 ma. A similar crystal which had not been previously irradiated on the cyclotron was placed on the opposite window of the x-ray tube. To compensate for any possible differences in the beam intensities between the two windows, the crystals were periodically interchanged giving each crystal the same length of time on each window. It was found that crystals which had been irradiated on the cyclotron could be colored much more readily than the ones which had not previously been irradiated and, furthermore, the crystals could be actually bodily colored. The crystals, which were about 3 mm thick, were cleaved after exposure to x-rays into three