

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 paper<sup>1</sup> an outline was given of the necessary<sup>7</sup> 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 Mo<sub>3</sub>P becomes superconducting near 7°K and Rh<sub>5</sub>P<sub>4</sub> 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.<sup>2,3</sup>

X-ray patterns showed that in general we were unable to obtain these phases completely pure. In the case of Mo<sub>3</sub>P, MoP was always present, and in Rh<sub>5</sub>P<sub>4</sub> we always detected Rh<sub>2</sub>P. Both MoP and Rh<sub>2</sub>P, however, can be prepared without any other phases present and neither becomes superconducting above 1.03°K.

(b) *The NiAs Structure*.—As mentioned before,<sup>1</sup> 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.<sup>4,5</sup> Assuming now that the transition temperature, if present, could be raised by enlarging the crystal lattice (as pointed out before<sup>1</sup>), 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<sub>0.75</sub>Pd<sub>0.25</sub>)As to (Ni<sub>0.12</sub>Pd<sub>0.88</sub>)As become superconducting above 1.06°K. The maximum transition temperature is reached for (Ni<sub>0.25</sub>Pd<sub>0.75</sub>)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 Rh<sub>3</sub>Se<sub>8</sub>, which is a well-defined compound,<sup>6</sup> becomes superconducting at 5.8°K.

According to Woehler<sup>7</sup> and Biltz,<sup>8</sup> the only compound in the Rh-Se system is supposed to be Rh<sub>2</sub>Se<sub>5</sub>. Now Rh<sub>2</sub>Se<sub>5</sub> 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 Rh<sub>3</sub>S<sub>8</sub> 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.<sup>1</sup> 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.<sup>1</sup> 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