

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

sections perpendicular to the direction of the x-ray beam. All three sections of the crystal, which had a previous proton irradiation, showed strong coloring, whereas, in crystals which had been exposed only to x-rays, only a thin surface layer of the first section was colored, the other two sections showing negligible color-center concentration. This indicates absence of any spurious effects due to scattered x-rays, etc.

Changes in density of the clear crystals were observed after cyclotron irradiation but before irradiation with x-rays. The observed decrease in density was about four times greater than had been previously reported for heavily² colored crystals. A more detailed quantitative study of these effects is underway.

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Coefficient of Expansion of Liquid Helium II

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WE have measured the coefficient of thermal expansion of liquid helium II from the λ point down to 0.85°K. The dilatometer was a closed system consisting of a copper chamber full of liquid helium attached to the lower end of a glass capillary in which the surface of the liquid could be viewed. The whole was immersed in a bath of liquid helium II and the procedure was to make a small measured change in bath temperature while observing the change in the position of the meniscus in the capillary. Temperatures below 1.2°K were obtained by pumping on the bath with a large diffusion pump and were measured by a carbon resistance thermometer which had been calibrated against the magnetic susceptibility of ferric alum.

Earlier density measurements¹ showed that the expansion coefficient is positive above the λ point but negative just below the λ point. Our extended measurements show that it becomes positive again below 1.12°K (Fig. 1). This was not unexpected,^{2,3} since liquid helium below 1°K is very similar to a Debye solid.⁴ In fact, the positive contribution which the phonons make to the expansion coefficient can be calculated from a form of Gruneisen's law,⁵

$$\alpha_{ph} = \frac{16\pi^5}{15} \frac{k^4}{h^2 c^3} \left(\frac{1}{c} \frac{\partial c}{\partial p} + \frac{1}{3\rho c^2} \right) T^3, \quad (1)$$

in which α_{ph} is the phonon coefficient of expansion, c the velocity of first sound, and $\partial c/\partial p$ the variation of this velocity with pressure. This expression reduces to

$$\alpha_{ph} = 1.08 \pm 0.04 \times 10^{-3} T^3 \text{ deg}^{-1}, \quad (2)$$

and is plotted as the dashed curve in Fig. 1.

If it is permissible to divide the measured coefficient of expansion α into separate phonon and roton contributions α_{ph} and α_r , then α_{ph} can be calculated from Eq. (2) and subtracted from α to give α_r . A calculation of $\alpha_r = -\rho(\partial S_r/\partial p)_T$, by using Landau's expression⁶ for S_r and keeping his notation, yields

$$\alpha_r = \frac{2(k\mu)^{1/2} p_0^2 \Delta}{(2\pi)^{1/2} \rho T^{1/2} h^2 c^2} \left(1 + \frac{3kT}{2\Delta} \right) \exp\left(-\frac{\Delta}{kT}\right) \times \left[\frac{1}{2} \frac{\rho}{\mu} \frac{\partial \mu}{\partial \rho} + 2 \frac{\rho}{p_0} \frac{\partial p_0}{\partial \rho} + \frac{\Delta}{\rho} \frac{\partial \Delta}{\partial \rho} - 1 - \frac{\rho}{\Delta} \frac{\partial \Delta}{\partial \rho} \frac{\Delta}{kT} \right] \times \left\{ 1 + \frac{\frac{3}{2}(kT/\Delta)^2}{1 + \frac{3}{2}kT/\Delta} \right\}. \quad (3)$$

Within the limits imposed by the experimental errors in the various quantities, this expression is consistent with the measurements below 1.6°K if

$$\left[\frac{1}{2} (\rho/\mu) (\partial \mu/\partial \rho) + 2 (\rho/p_0) (\partial p_0/\partial \rho) + (\rho/\Delta) (\partial \Delta/\partial \rho) \right] \sim -1.5$$

and $(\rho/\Delta) (\partial \Delta/\partial \rho) \sim -0.65$.

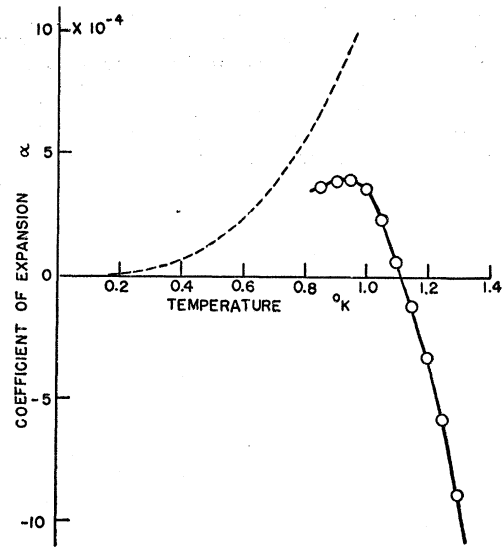


FIG. 1. The coefficient of thermal expansion of liquid helium II below 1.4°K. O, Experimental. ---, Phonon contribution.

Integrating α gives an accurate curve for the variation of density with temperature, and again this may be divided into phonon and roton parts,

$$\rho = \rho_0 + \delta\rho_{ph} + \delta\rho_r. \quad (4)$$

By calculating $\delta\rho_{ph}$ from (2) and using it to derive $\delta\rho_r$ from (4), it appears that $\delta\rho_r$ is very nearly a linear function of the density of the normal component ρ_n . It is not possible to say whether this fact has any more fundamental significance than the approximate agreement with Landau's theory. A careful comparison of theory and experiment must await more accurate values of certain quantities, in particular the entropy, which at present is uncertain to about 10 percent.⁶

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Temperature Measurement below 1°K*

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USUALLY the thermometric parameters used for temperature measurements below 1°K are magnetic in character—the susceptibility, the remanence, and the area of the hysteresis loop have been so used. By carrying out thermodynamic cycles or by equivalent means, these parameters can be calibrated absolutely.¹ For temperatures down to a little way below the Curie point the results are most often presented as a $T-T^*$ relation, T being the absolute temperature, T^* the Curie temperature proportional to the reciprocal of the susceptibility. When a secondary thermometer, such as a resistance thermometer in thermal contact with the paramagnetic salt, is to be calibrated absolutely, it is usual to calibrate the resistance against T^* and then to apply the $T-T^*$ relation, usually determined in another experiment or taken from previously published data. Though there is a good deal of evidence