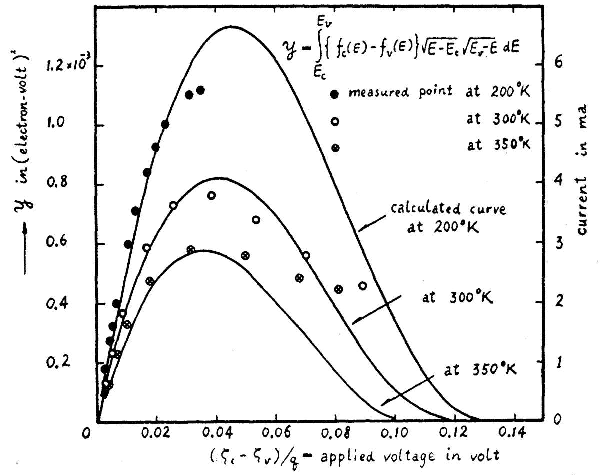

FIG. 3. Comparison of the current-voltage curves calculated with the measured points at 200°K, 300°K, and 350°K.

$I_{c\to v}$ from the conduction band to the empty state of the valence band should be detail-balanced. Expressions for $I_{c\to v}$ and $I_{v\to c}$ might be formulated as follows:

$$I_{c\to v}=A\int_{E_c}^{E_v} f_c(E)\rho_c(E)Z_{c\to v}\{1-f_v(E)\}\rho_v(E)dE,$$

$$I_{v\to c}=A\int_{E_c}^{E_v} f_v(E)\rho_v(E)Z_{v\to c}\{1-f_c(E)\}\rho_c(E)dE,$$

where $Z_{c\to v}$ and $Z_{v\to c}$ are the probabilities of penetrating the gap (these could be assumed to be approximately equal); $f_c(E)$ and $f_v(E)$ are the Fermi-Dirac distribution functions, namely, the probabilities that a quantum state is occupied in the conduction and valence bands, respectively; $\rho_c(E)$ and $\rho_v(E)$ are the energy level densities in the conduction and valence bands, respectively.

When the junction is slightly biased positively and negatively, the observed current I will be given by

$$I=I_{c\to v}-I_{v\to c}=A\int_{E_c}^{E_v}\{f_c(E)-f_v(E)\}Z\rho_c(E)\rho_v(E)dE.$$

From this equation, if Z may be considered to be almost constant in the small voltage range involved, we could calculate fairly well the current-voltage curve at a certain temperature, indicating the dynatron-type characteristic in the forward direction, as shown in Fig. 3.

Further experimental results and discussion will be published at a later time. The author wishes to thank Miss Y. Kurose for assistance in the experiment and the calculations.

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[1] A. H. Wilson, Proc. Roy. Soc. (London) **A136**, 487 (1932); J. Frenkel and A. Joffe, Physik. Z. Sowjetunion **1**, 60 (1932); L. Nordheim, Z. Physik **75**, 434 (1932).

[2] McAfee, Ryder, Shockley, and Sparks, Phys. Rev. **83**, 650 (1951); C. Zener, Proc. Roy. Soc. (London) **145**, 523 (1934).

[3] S. L. Miller, Phys. Rev. **99**, 1234 (1955); A. G. Chynoweth and K. G. McKay, Phys. Rev. **106**, 418 (1957).

Ferromagnetism of a Zirconium-Zinc Compound

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A COMPOUND of two superconducting elements, zirconium and zinc, with the approximate composition 1 Zr:2 Zn, has been found to become ferromagnetic below 35°K. The saturation moment is about 0.13 Bohr magneton per molecule (Fig. 1).

There are only a few ferromagnetic elements. They are Fe, Co, Ni, and some of the rare earth metals with partly empty 4*f* shells. No ferromagnetic intermetallic compounds are known that do not contain any of the afore-mentioned elements or Cr and Mn. The last two also occur in antiferromagnetic modifications. This has led to the tacit assumption that no ferromagnetism could occur in an intermetallic compound unless it contained at least one strongly paramagnetic element.

When one considers the fact that both zirconium and zinc are not magnetic (in addition to being superconductors), the ferromagnetism of this compound is therefore a rather remarkable phenomenon. It indicates that ferromagnetic and perhaps also antiferromagnetic compounds may be formed by the combination of many

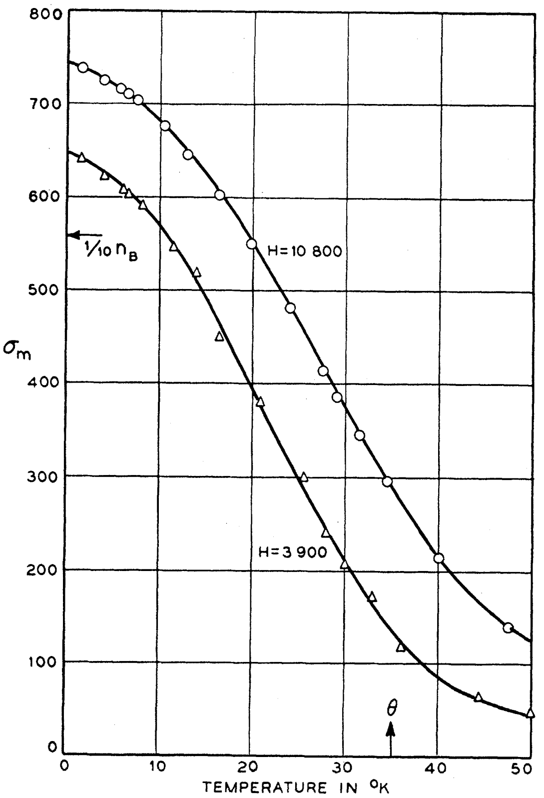

FIG. 1. Saturation moment *vs* temperature of a zirconium-zinc compound with the approximate composition of 1:2.

more metals than had been supposed until now. It will be interesting to see whether this material is superconducting.[1] E. A. Wood has identified our material with that of Pietrokowsky,[2] who determined that its structure was the cubic $MgCu_2$ structure.

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[1] V. L. Ginzburg, Zhur. eksptl. i teort. Fiz. **31**, 202 (1956) [translation: Soviet Phys. JETP **4**, 153 (1957)].
[2] P. Pietrokowsky, J. Metals **6**, 219 (1954).

Vacancy Diffusion in Binary Ordered Alloys

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SLIFKIN and Tomizuka[1] have suggested that vacancy diffusion in certain well-ordered binary alloys should lead to equal self-diffusion coefficients for the two components of the alloy. It was assumed, as it will be in all that follows, that (1) the lattice of the alloy may be subdivided into two sublattices such that nearest neighbor sites of a site on one sublattice all lie on the other sublattice, the state of perfect order of the AB alloy being such that each sublattice is occupied by atoms of one kind, and (2) the only mechanism for atom interchange is by vacancy jumps from a site to a nearest neighbor site. The argument is simply that, in the course of $2m$ vacancy jumps through the well-ordered AB lattice, m A atoms and m B atoms are each displaced an equal distance: it is inferred that the self-diffusion coefficients of the two components of the alloy are equal.

This suggestion has been criticized by Lidiard[2] who points out that such vacancy tracks do not satisfy the equilibrium requirements for the alloy. There are, however, as has been remarked by Huntington,[3] certain cyclic vacancy tracks which could produce diffusion without creating disorder. Although such highly correlated processes might seem at first sight very improbable, we shall show that, at sufficiently low temperatures, they provide the dominant mechanism for diffusion.

Consider a vacancy supposed initially to be at an a site in an otherwise perfectly ordered body-centered cubic AB crystal. A jump of the vacancy into one of the nearest neighbor b sites disorders a B atom with consequent increase in configuration energy and, for temperatures low compared to the critical temperature, will almost always be followed by a jump of the vacancy back into its original position. Two successive jumps of the vacancy away from the original position, involving the disordering of two atoms and consequently a greater increase in configurational energy, will occur much less frequently and such jumps also will tend to be immediately retraced: the vacancy is strongly bound to its initial position. It follows that a configuration in which a vacancy has a perfectly ordered local environment is, at sufficiently low temperatures, very stable. Further, none of these processes involving jumps away from the initial position followed by retracing of these jumps give rise to net diffusion.

Eventually the vacancy will, in some series of jumps, either return to its initial stable position by a process not depending on retracing of jumps, or escape to a different stable position. Either process results in net displacements of the atoms of the alloy. In fact, the escape to a new stable position is the most probable process. The vacancy will be in a position to escape from an initial stable position if it makes three successive jumps around a square of four nearest neighbor sites in a (111) plane: the vacancy is then just as likely to make a further forward jump around the square as a backward jump. If the vacancy makes the forward jump, however, it will then be bound to a *new* stable position at the site on the square diagonally opposite the initial site. In going from the initial to the final stable configuration, the vacancy makes six jumps around the sides of the square. The net result so far as diffusion is concerned is that if the initial vacancy site was an $a(b)$ site, two $B(A)$ atoms will have interchanged places, so that each has been displaced a distance equal to the diagonal of the square considered, and one $A(B)$ will have moved the same distance. No net disordering occurs.

In order to execute any other nontrivial series of jumps starting and ending in a stable state, the vacancy must pass through a configuration of higher energy than any occurring in the six-jump process described. Moreover, the increase in the number of equivalent processes will not compensate for this increase in configurational energy at sufficiently low temperatures. At sufficiently low temperatures, then, we may regard diffusion as taking place solely by the six-jump process described. It should be noted here, however, that although other cyclic processes make no appreciable contribution to diffusion, they constitute mechanisms by which semipermanent local regions of disorder may be created and destroyed and hence play a part in maintaining the equilibrium disorder. Since it may be shown that Bardeen-Herring type correlations between successive jumps of A and B atoms are approximately the same, the mean square displacement of $B(A)$ atoms due to an $a(b)$ vacancy making a series of six-jump processes will be approximately twice that of $A(B)$ atoms. At sufficiently low temperatures, then, we expect the value of the ratio of self-diffusion, G, of A to B atoms to lie between 2 and $\frac{1}{2}$, the precise value being given by

$$G=D_B/D_A=(2n_aw_a+n_bw_b)/(2n_bw_b+n_aw_a),$$

where n_a and n_b are equilibrium concentrations and w_a and w_b are frequencies for the six-jump process for the two kinds of vacancy.