

FIG. 1. Concentration versus distance for copper nuclei (A) and thermal acceptors (B) in germanium (heated two minutes at 825°C).

ment with the value at 825°C calculated from  $D=0.02 \exp(-12000/RT)$ , which has been found to apply approximately to thermal acceptor diffusion.<sup>2</sup>

In another set of experiments, six of the germanium specimens were immersed in the radioactive copper nitrate solution for two minutes and heated in helium at 1 atmosphere at temperatures

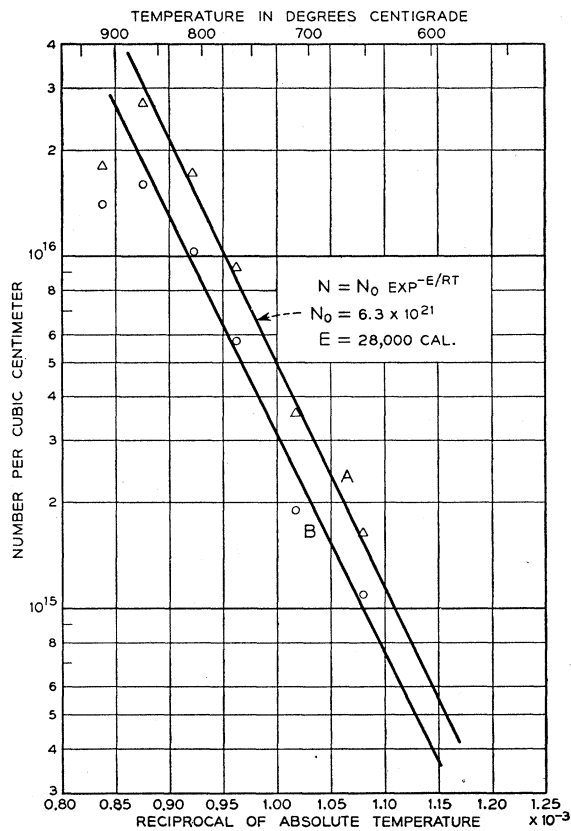


FIG. 2. Temperature variation of equilibrium concentration of copper nuclei (A) and added acceptors (B) in germanium.

of 654, 712, 765, 812, 868, and 919°C for 16 hours, 1 hour, 1 hour, 50 minutes, 40 minutes, and 30 minutes, respectively. These times were sufficient to ensure that the specimens were within at least 5 percent of saturation. Resistivities were determined after removal of excess copper from the surfaces and the copper concentrations then measured by crushing the entire specimens and counting the radioactivity. The results plotted in Fig. 2 are the same within the limit of error and the uncertainty in the value of the mobility.<sup>7</sup> Deviations from the theoretical diffusion curves at low concentrations may be due to diffusion from the rear surfaces.

Heat treatments at 500°C have been carried out on *p*-type germanium (originally 13.5 ohm-cm *n*-types) which had been saturated with Cu<sup>64</sup> at 924°C. After 18 and 48 hours the copper concentrations (on separate specimens) were  $3.0 \times 10^{16}$  and  $1.4 \times 10^{16}$  respectively compared with the original  $3.0 \times 10^{16}$ . The 500°C specimens showed high surface activities indicating that some copper had come to the surface. The 18-hour specimen was still partly *p*-type, whereas the 48-hour specimen had an *n*-type resistivity of 20 ohm cm. Thus, most of the copper remained in the crystal even though it returned to nearly its original resistivity. This indicates that the copper is no longer in solid solution after annealing, but has precipitated as a separate phase.

Experiments on silicon at 1100°C show that copper diffuses into it at a rate comparable to that found for germanium and that an increase in hole conductivity occurs. As yet, no direct correlation of the numbers of copper atoms with the number of added holes has been made.

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<sup>1</sup> H. C. Theuerer and J. H. Scaff, *J. Metals* **191**, 59 (1951).

<sup>2</sup> Fuller, Theuerer, and Van Roosbroeck, *Phys. Rev.* **85**, 678 (1952).

<sup>3</sup> Assuming one conducting hole per acceptor.

<sup>4</sup> Prepared at Brookhaven National Laboratory, Upton, New York.

<sup>5</sup> G. K. Teal and J. B. Little, *Phys. Rev.* **78**, 647 (1950).

<sup>6</sup> Calculated according to J. L. Ham, *Trans. Am. Soc. Metals* **31**, 849 (1943).

<sup>7</sup> J. R. Haynes and W. Shockley [*Phys. Rev.* **81**, 835 (1951)] give values of 3600 and 1700 cm<sup>2</sup>/volt-sec for electrons and holes respectively. We have applied corrections for the variation with resistivity supplied by G. L. Pearson and P. P. Debye of these Laboratories.

### Impurity Effects in the Thermal Conversion of Germanium

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IT was shown by Theuerer and Scaff<sup>1</sup> that polycrystalline *n*-type germanium is converted to or toward *p*-type when heated for a few minutes above about 600°C, and the process is reversed when the material is heated for about 24 hours at 500°C. Theuerer, Fuller, and Slichter<sup>2</sup> have found that the same effects occur with single-crystal germanium, except that the original resistivity is restored only after several days of heating at 500°C. It might be expected, then, that with the high temperatures encountered in the crystal-growing process of Teal and Little,<sup>3</sup> there would be an appreciable and variable concentration of thermally-induced acceptors. The present studies, however, have revealed no thermal acceptors as a consequence of the growing process and have shown that conversion may be associated with the presence of impurities on the germanium surface prior to heating.

In these experiments, a crystal of very high purity germanium (resistivity > 45 ohm-cm) was partly grown (in hydrogen), and then the growth was halted, keeping the crystal in contact with the hot melt for a prolonged period (in one case an hour, in another, 2 hours). The growth was then resumed and completed in about ten minutes. A study of the resistivity throughout the length of the crystal showed no detectable difference between the first portion, which had undergone prolonged heating, and the second, which

TABLE I. The concentration of copper atoms and holes in germanium containing radioactive copper.

Sample	Cu atoms per cc	Holes per cc	Ratio Cu/holes
1	$2.0 \times 10^{14}$	$1.7 \times 10^{14}$	1.2
2	$9.0 \times 10^{14}$	$8.8 \times 10^{14}$	1.0
3	$3.6 \times 10^{14}$	$3.9 \times 10^{14}$	0.9

had been hot only briefly. The material was all *n*-type, according to measurements of the thermal emf.

In another experiment the crystal was grown to the halfway point, and was removed from the crystal growing machine. The partly-grown crystal was immersed briefly in pure water (doubly distilled in Pyrex), which was allowed to evaporate from the surface of the germanium. The crystal was then returned to the machine and was held in contact with the melt for 30 minutes, whereupon the growth was resumed as above. Again there was no evidence of conversion. Nor was there any conversion in a similar experiment in which the partly-grown crystal was exposed to the air for 15 hours, instead of being immersed in pure water.

Fuller had observed<sup>2</sup> that conversion occurred when copper salts were present on the surface of a cut and lapped germanium wafer prior to heating. Hence the present experiment on an uncut crystal was performed using a dilute solution of copper sulfate (0.001 atomic percent) in pure water, followed as before by heating for 30 minutes in contact with the melt. Extensive conversion, with resistivity as low as 4 ohm-cm along the growth axis, occurred in that part of the crystal which had been heated, but no conversion occurred in the part subsequently grown. It was found that for sufficiently dilute copper sulfate solutions (somewhat more dilute than 0.001 atomic percent), the degree of conversion depended upon the concentration of the solution and the time that the crystal was immersed. This suggests that a surface reaction with the germanium is a necessary step in conversion.

In a similar experiment, using a solution containing the radioactive isotope  $\text{Cu}^{64}$ , copper was found to have entered the germanium. Tracer measurements of the copper concentration, performed by Struthers, and resistivity measurements indicate the following relation between copper concentration and hole concentration in three specimens from the same crystal,<sup>4</sup> (Table I).

The calculation of hole concentrations from resistivity measurements involved use of the value  $1700 \text{ cm}^2/\text{volt-sec}$  for the hole mobility. The aggregate experimental error was probably about 30 percent.

These results, together with the studies by Fuller and Struthers<sup>5</sup> on the diffusion of copper, are in keeping with the proposition that thermal conversion may be associated with the rapid diffusion of copper into the germanium.

<sup>1</sup> H. C. Theuerer and J. H. Scaff, *J. Metals* **191**, 59 (1951).

<sup>2</sup> Unpublished studies.

<sup>3</sup> G. K. Teal and J. B. Little, *Phys. Rev.* **78**, 647 (1950).

<sup>4</sup> Similar values for the ratio of copper concentration to hole concentration have been found by J. A. Burton in germanium crystals grown from a melt containing radioactive copper.

<sup>5</sup> C. S. Fuller and J. D. Struthers, *Phys. Rev.* **87**, 526 (1952).

### Decay Scheme of ${}_{21}\text{Sc}^{48}$

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THE decay scheme of  ${}_{21}\text{Sc}^{48}$  is of interest because in the *jj*-coupling shell model this nucleus is a particularly simple configuration. It represents the coupling of a single  $1f_{7/2}$  proton with a single  $1f_{7/2}$  neutron-hole. Calculations with product wave functions and static central-force interactions between nucleons indicate that in such cases the ground state has a spin that is either the maximum possible or one unit less than this.<sup>1</sup> Maximum spin,  $I = j_1 + j_2$ , results from use of an infinite range spatial de-

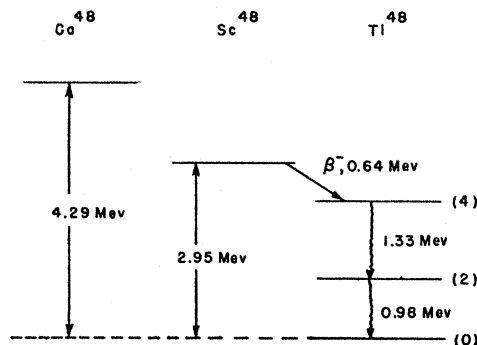


FIG. 1. Experimental energy differences at mass number 48. Probable spins of the  $\text{Ti}^{48}$  levels are given in parentheses.

pendence in the interaction, while the use of a delta-function range dependence gives  $I = j_1 + j_2 - 1$ . The competing levels will cross somewhere between these limits, the indication from the measured spins of the analogous cases  ${}_{17}\text{Cl}^{36}$  and  ${}_{19}\text{K}^{40}$  being that the delta-function result is more likely.

Therefore the spin of  $\text{Sc}^{48}$  is expected to be 6 or possibly 7, which is also in agreement with the prediction of Nordheim's rules<sup>2</sup> for odd-odd nuclei. The decay scheme of  $\text{Sc}^{48}$  shows an allowed beta decay ( $\log ft \sim 5.4$ ) followed by two gammas in cascade as in Fig. 1. The spin assignments of the levels of  $\text{Ti}^{48}$  are probably the same as in the isotope  $\text{Ti}^{46}$  where gamma-gamma correlation<sup>3</sup> is consistent with the assignments  $I = 0, 2, 4$ . Therefore, the fact that the beta-decay is allowed is not consistent with the assignment of 6 (or 7) for the spin of  $\text{Sc}^{48}$ .

However, recent measurements<sup>4</sup> of the masses of  $\text{Ca}^{48}$  and  $\text{Ti}^{48}$  give a difference in mass of  $4.29 \pm 0.15$  Mev, which means that if the decay scheme of  $\text{Sc}^{48}$  is correct,  $\text{Ca}^{48}$  should be unstable to negative beta decay to  $\text{Sc}^{48}$  with an energy of  $1.35 \pm 0.2$  Mev as indicated in Fig. 1. This fact has been pointed out recently,<sup>5</sup> and a search for this beta-activity led to negative results with a lower limit of  $2 \times 10^{16}$  years for the lifetime. From calculation and comparison with the similar isotopes  ${}_{21}\text{Sc}^{44}$  and  ${}_{21}\text{Sc}^{46}$  which have low-lying isomeric states, one would expect that  $\text{Sc}^{48}$  has an excited state of low spin, to which  $\text{Ca}^{48}$  could readily decay, within 0.5 Mev of the ground state. The fact that no activity is found even though 1.35 Mev is available is puzzling.

If, on the other hand, there were another gamma-ray of sufficient energy present in cascade with the known gammas in the decay scheme of  $\text{Sc}^{48}$ , the situation could be understood. For then the spin of 6 (or 7) would not be inconsistent with the allowed beta followed by three gammas; and simultaneously there would be very little energy left for the decay involving  $\text{Ca}^{48}$ , as a result of which the large spin change present would lead to such a long lifetime that observation would be extremely difficult.

<sup>1</sup> D. Kurath, *Phys. Rev.* **87**, 218 (1952).

<sup>2</sup> L. W. Nordheim, *Revs. Modern Phys.* **23**, 322 (1951).

<sup>3</sup> E. L. Brady and M. Deutsch, *Phys. Rev.* **74**, 1541 (1948).

<sup>4</sup> Collins, Nier, and Johnson, Jr., *Phys. Rev.* **84**, 717 (1951); also further results to be published.

<sup>5</sup> J. W. Jones and T. P. Kohman, *Phys. Rev.* **85**, 941 (1952).

### Gamma-Rays from $\text{Sc}^{48}$

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AS indicated in the preceding Letter,<sup>1</sup> the question of a missing amount of energy (1–1.5 Mev) in the  $\text{Ca}^{48}$ ,  $\text{Sc}^{48}$ , and  $\text{Ti}^{48}$  masses and decay schemes may be resolved by finding a beta process in  $\text{Ca}^{48}$  or by finding a third gamma-ray in the  $\text{Sc}^{48}$  scheme. We have looked for and found the latter.