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Letters to the Editor

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Clustering Phenomena in Solid Solution

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WHEN a binary solid solution decomposes on cooling and a precipitate forms, the new phase has a definite crystallographic orientation with respect to the matrix as well as habit plane which separates the matrix from the new phase. In many cases in which this habit plane and orientation have been observed, both can be explained in terms of mechanism of transformation or in terms of lattice coherency. The coherency requirement takes into account the fact that the atoms on the boundary tend to be least disturbed. In the case of silver-copper alloys, however, these two factors obviously do not play a significant role because on both ends of the equilibrium system—that is, for copper precipitating out of silver and silver precipitating out of copper—the orientation relationship between the two phases is identical; but on the silver-rich end of the system the habit plane is the (111) plane, while at the other end it is the (100) plane.

This difference can be explained as a result of the structure of the solid solution. A random solution, even in condition of perfect randomness, has a number of areas in which, because of statistical fluctuation, the concentration of the solute atoms is particularly high. Let us consider three solute atoms which tend to make as many nearest neighbors among themselves as possible and which are larger than the atoms of the matrix. It is possible, using fairly simple assumptions, to estimate the energy of elastic deformation of the matrix surrounding the three atoms as a function of the index of the crystallographic plane determined by these atoms. It turns out that the elastic energy is greatest for the (111) plane, somewhat smaller for the (100), and still less for the (110) plane. The same sequence of planes can be obtained using a treatment similar to that of Nabarro[1] which he used in the case of an isotropic medium. On the (111) plane the three atoms form three nearest neighbors, on the (100) plane two neighbors, and on the (110) plane only one nearest neighbor. Thus, the (111) plane, although most favorable from the point of view of bond formation, is less favorable from the point of view of elastic energy. Since the absolute values of the two types of energy are difficult to estimate, we can only conclude that in a copper-rich alloy on the (100) plane the balance of the two energies is optimum. With lower bond energies or higher deformation energies one might expect the habit plane to be the (110) plane. On the silver-rich end of the system, on the other hand, where the precipitate atoms are smaller than the matrix atoms, this elastic energy functions to a much lesser extent because the matrix is less deformed and also the binding of the copper atoms is stronger than that of the silver atoms as evidenced in various atomic and metallic properties. Thus, here the (111) plane is most favorable.

Nabarro's work indicates that crystals of atoms which do not fit into the lattice prefer to form disks or plate-like shapes rather than spherical agglomerates or needles. The treatment here discussed indicates that these plates prefer to be oriented with respect to the crystal lattice. Many other phenomena can be explained on a similar basis. Among them is the influence of silicon on the mechanism of the deformation of alpha-iron, which indicates that silicon preferentially blocks planes (211) and (123) so that a slip can occur only on the (110) planes. Further such effects as the (210) habit plane in the precipitation of Fe_4N from alpha-iron can be explained. A more complete treatment will be published later.

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[1] N. F. R. Nabarro, Proc. Phys. Soc. 52, 90 (1940); Proc. Roy. Soc. 175, 519 (1940).

On the Isotopic Composition of Meteoritic and Terrestrial Gallium

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CONTINUING our comparisons of the isotopic composition of elements occurring in meteorites with those occurring in the earth's crust,[1] the isotopic composition of gallium has been studied. A sample of commercial gallium, converted to the nitrate, was used as the terrestrial standard. Several milligrams of meteoritic gallium were isolated from the Canyon Diablo meteorite for comparison. The Canyon Diablo meteorite, having as its major constituent the element iron, contains on the average 38 ppm of gallium.[2] A kilogram of the meteorite was dissolved in concentrated HCl, the acidity was adjusted to $6M$, and the solution was ether-extracted. Under such conditions gallium is ether-soluble. The major portion of the iron is in the ferrous stage and is not ether-soluble, although some of the iron is unavoidably oxidized by air and accompanies the gallium in the ether layer. The ether solution of gallium, containing some iron, was extracted into water, the iron was reduced to the ferrous stage, and the solution was again ether-extracted. The gallium was finally precipitated as gallium 8-hydroxy quinoline, following which it was converted to the nitrate.

The mass-spectrometer technique used in the analysis of these samples was that described by some of us in connection with studies of lanthanum and cerium.[3] Aliquots of the samples were pipetted onto the filament of a surface ionization type source as a nitric acid solution. Gentle heating served to convert the nitrate to an adherent oxide coat. Emission of Ga^+ ions began at approximately 650°C. No compound gallium ions were observed throughout the course of the experiment. The results obtained, along with the results of Sampson and Bleakney,[4] are given in Table I.

TABLE I. Abundance ratio of Ga^{69}/Ga^{71} from terrestrial and meteoritic sources.

Investigator	Source	Ga^{69}/Ga^{71} ratio
Sampson and Bleakney[4]	Terrestrial	1.58
This work	Terrestrial	1.510
This work	Meteoritic	1.509

The samples were four times introduced, each for purposes of precision in the comparison of the isotopic ratios. Evaluation of errors shows that the isotopic ratios of the terrestrial and meteoritic samples are the same to within two-tenths of one percent. The absolute ratios given in Table I are the average values of 250 individual results. As a result of possible fractionations and discriminations they are good to three-fourths of one percent. It is apparent, however, that our value is not compatible with that of Sampson and Bleakney. This may be due to voltage effects in the Sampson and Bleakney measurements which were avoided in our observations.

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[1] H. Brown and M. G. Inghram, Phys. Rev. 72, 347 (1947).
[2] H. Brown and E. Goldberg (work to be published).
[3] M. G. Inghram, R. J. Hayden, and D. C. Hess, Jr., Phys. Rev. 72, 967 (1947).
[4] M. B. Sampson and W. Bleakney, Phys. Rev. 50, 456 (1936).

Long-Lived Tc Activities Produced by Deuteron Bombardment of Separated Mo Isotopes*

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IN two earlier letters (April 30, 1948 and May 26, 1948) a preliminary report was given on a group of Tc activities (element 43) produced by irradiation of the separated Mo isotopes with ~16-Mev deuterons. It is now possible to report confirmatory evidence on the mass assignment of several of the known long-lived Tc activities, based on the results of bombardments of the various separated Mo isotopes with *ca.* 22-Mev deuterons from the Berkeley 60-inch cyclotron.

4.2-day Tc. This Tc activity[1,2] was produced in greatest yield from the deuteron bombardment of Mo enriched in Mo^{96} and decayed with a half-life of 4.2±0.1 days (Fig. 1). This result serves to confirm the assignment of the 4.2-day Tc to Tc^{96}. Gamma-rays of 0.8±0.1-Mev energy as well as 17–18-kev x-rays were observed. Charged particles of 0.64-Mev energy[2] were not found, however.

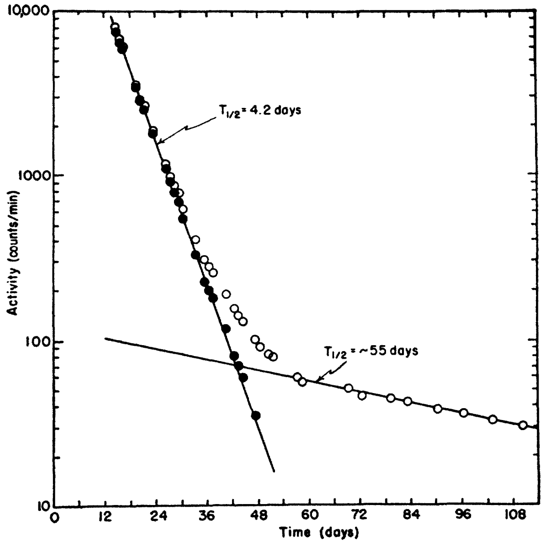

FIG. 1. Decay curve of the 4.2-day Tc activity produced by deuteron bombardment of Mo enriched in Mo^{96}.

50–60-day Tc. The previously studied 50–60-day Tc^{2-4} was produced in greatest yield from the deuteron bombardment of Mo enriched in Mo^{95}. The decay curve (Fig. 2A) gave an apparent half-life of 59 days. This value will be reduced slightly by the subtraction of a 90-day component which is almost certainly present. The radiations found associated with this period were a 0.8±0.1-Mev γ-ray, a 0.24±0.05-Mev γ-ray, and x-rays characteristic of the

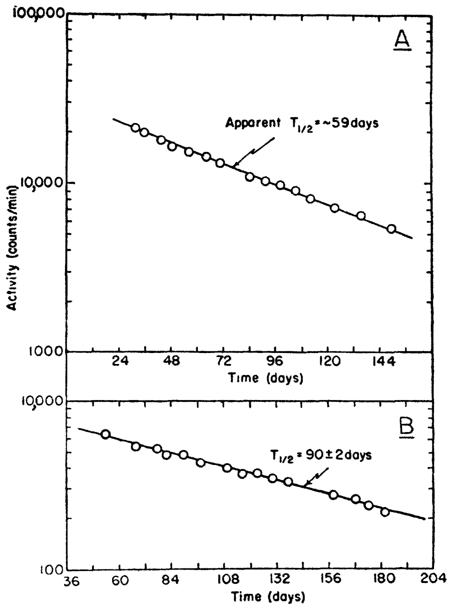

FIG. 2. A. Decay curve of the 50–60-day Tc activity produced by deuteron bombardment of Mo enriched in Mo^{95}. B. Decay curve of the 90-day Tc activity produced by deuteron bombardment of Mo enriched in Mo^{97}