

falls indicates an exponential time-decay of the radium content. The negative exponent increases with the rate of precipitation, as the scavenging action becomes greater. The maximum radium content recorded was 1.5×10^{-12} c./l. When continuous rainfall was recorded, however, in most cases the last portion carried negligible activity ($< 10^{-14}$ c./l.).

We thank Dr. G. Ramaswamy for his help in analysing our data.

PARTHA BANERJI
S. D. CHATTERJEE

Department of Physics,
Jadavpur University,
Calcutta.

¹ Damon, P. E., and Kuroda, P. K., *Trans. Amer. Geophys. Union*, **35**, 208 (1954).

² Chatterjee, S. D., Mondal, S. K., Das, S. K., and Ghosh, N. C., *Ind. J. Phys.*, **38**, 635 (1964).

³ Hahn, O., *Applied Radiochemistry*, 81 (1936).

⁴ Kropf, Fritz, *Mitteilungen des Institutes für Radiumforschung*, 429 (Wien, 1939).

Cyclic Pattern of Metallic Crystal Structures

The three principal crystal structures of the metallic elements, the face-centred cubic (f.c.c.), the body-centred cubic (b.c.c.) and the hexagonal close-packed (h.c.p.), follow a cyclic pattern as sub-shells are filled with electrons. The preferred structure changes from f.c.c. to h.c.p. to b.c.c. for the half-filled sub-shell. As the sub-shell continues to fill, the trend is reversed.

When a sub-shell is either empty or full, atoms pack as spheres and the f.c.c. structure predominates. The rare gases (p^6), calcium and strontium (s^2), the cobalt, nickel and copper group metals (d^{10}) and ytterbium (f^{14}) adopt this structure. The high packing density and high symmetry (low entropy) aspects of the f.c.c. structure produce the lowest energy environment for the packing of spherically symmetric atoms. The major exceptions to this occur among the alkaline earth metals where the effect of losing an s -electron to the conduction band is most pronounced.

As the s , d and f sub-shells start to fill, atoms gain a net electron spin. The crystal structure distorts to permit adjustment of interatomic distances. The crystal energy is lower if two sets of interatomic distances are provided, and atoms with antiparallel spins are permitted to maintain a closer approach than atoms with parallel spins. Classical examples of this type of spin interaction are the formation of the hydrogen molecule and the sign of the Slater¹ exchange integral. The f.c.c. structure does not provide two sets of interatomic distances. Every atom has nearest neighbours which are nearest neighbours of each other. No assignment of spins can satisfy the requirement of maintaining different interatomic distances for parallel and antiparallel interaction. The h.c.p. structure, when c/a is less than the theoretical value for closest packing 1.633, permits nearest neighbours to have antiparallel spins and next nearest neighbours to have parallel spins. Six nearest neighbours occupy the corners of a trigonal prism at a distance less than the lattice parameter ' a '. Next nearest neighbours occupy the corners of a hexagon at a distance equal to the lattice parameter ' a '. The h.c.p. structure with c/a less than 1.633 is found where metal atoms have a weak net spin. The energy gained in providing two sets of interatomic distances makes up for the energy lost in a lower packing density and lower symmetry. Weak net spins occur when shells just begin to fill and when they are almost filled. The scandium and titanium groups of metals have this structure. They represent the low net spin as the d -shell begins to fill. It occurs again in the almost filled d -shells with the metals technetium, ruthenium, rhenium and osmium. The structure is also observed among early $4f$ metals lanthanum to samarium

and the late $4f$ metals gadolinium to thulium. All these h.c.p. metals have c/a ratios less than 1.633. Two metals, zinc and cadmium, have c/a ratios greater than 1.85. This large departure has been explained on the basis of dp^2 hybrids².

The net spin reaches its maximum value when the sub-shell is half-filled. The alkali metals, lithium to caesium, the refractory metals of the titanium, vanadium and chromium groups and europium have half-filled s , d and f shells, respectively. These metals crystallize in the b.c.c. structure. Zener³ observed the tendency of the d sub-shell metals of high net electron spin to crystallize in a structure which permits nearest neighbours to have antiparallel spins. He explained how the b.c.c. structure fulfilled this requirement. Each atom in the b.c.c. structure is surrounded by eight nearest neighbours located at the corners of a cube. Next nearest neighbours are located at the centre of six adjacent cubes sharing the cube faces. The packing density is now about 9 per cent less than in the f.c.c. structure. The energy saved in providing two sets of interatomic distances for parallel and antiparallel electron spin interactions more than compensates for the lower packing densities.

It is a matter of conjecture whether or not the requirement of two sets of interatomic distances to accommodate parallel and antiparallel spin interaction requires a spin ordering in the structure. Neutron diffraction investigations of such systems have been discussed extensively⁴. Briefly, attempts to see spin ordering in b.c.c. elements by neutron diffraction have failed. However, the question remains whether the resonance frequency of exchange is too rapid to be resolved by neutron diffraction techniques.

In summary, the crystal structures of metallic elements possessing a net electron spin have their lowest energy when in a structure which provides a closer approach for atoms with antiparallel net electron spin than for atoms with parallel spin. As the s , d and f sub-shells fill, the equilibrium crystal structures follow the cyclic pattern f.c.c.-h.c.p.-b.c.c.-h.c.p.-f.c.c. When the sub-shells are empty or completely filled and the net spin is zero, the f.c.c. structure is preferred. When the net electron spin reaches a maximum, metallic elements tend to assume the b.c.c. structure. For intermediate values of net spin, they prefer the h.c.p. structure with c/a less than the theoretical value of 1.633. Exceptions to the rule occur among the alkaline earth metals, the actinides, and the lighter elements lithium, sodium, manganese and iron. In general, however, metals follow the cyclic pattern as closely as the anions follow the Hume-Rothery $8-N$ rule.

ALBERT J. CORNISH*

Research Laboratories,
United Aircraft Corporation,
East Hartford, Connecticut.

* Present address: Royal Typewriter Company, Inc., Research and Development, 1031 New Britain Avenue, West Hartford, Connecticut.

¹ Slater, J. C., *Phys. Rev.*, **36**, 57 (1930).

² Wallace, W. E., *J. Chem. Phys.*, **23**, 2281 (1955).

³ Zener, C., *Phys. Rev.*, **81**, 440 (1951).

⁴ Shull, C. G., and Wollan, E. O., in *Solid State Physics, Advances in Research and Applications*, edit. by Seitz, F., and Turnbull, D., **2**, 137 (Academic Press, Inc., New York, 1956).

METALLURGY

Formation of Intergranular Voids and Cracks in an Irradiated Austenitic Steel tensile-tested in the Temperature Range 650°-850° C

THE elevated temperature embrittlement induced in austenitic steels by neutron irradiation is now well known^{1,2}. Characteristic features are the intergranular mode of fracture in a tensile test and the marked reduction