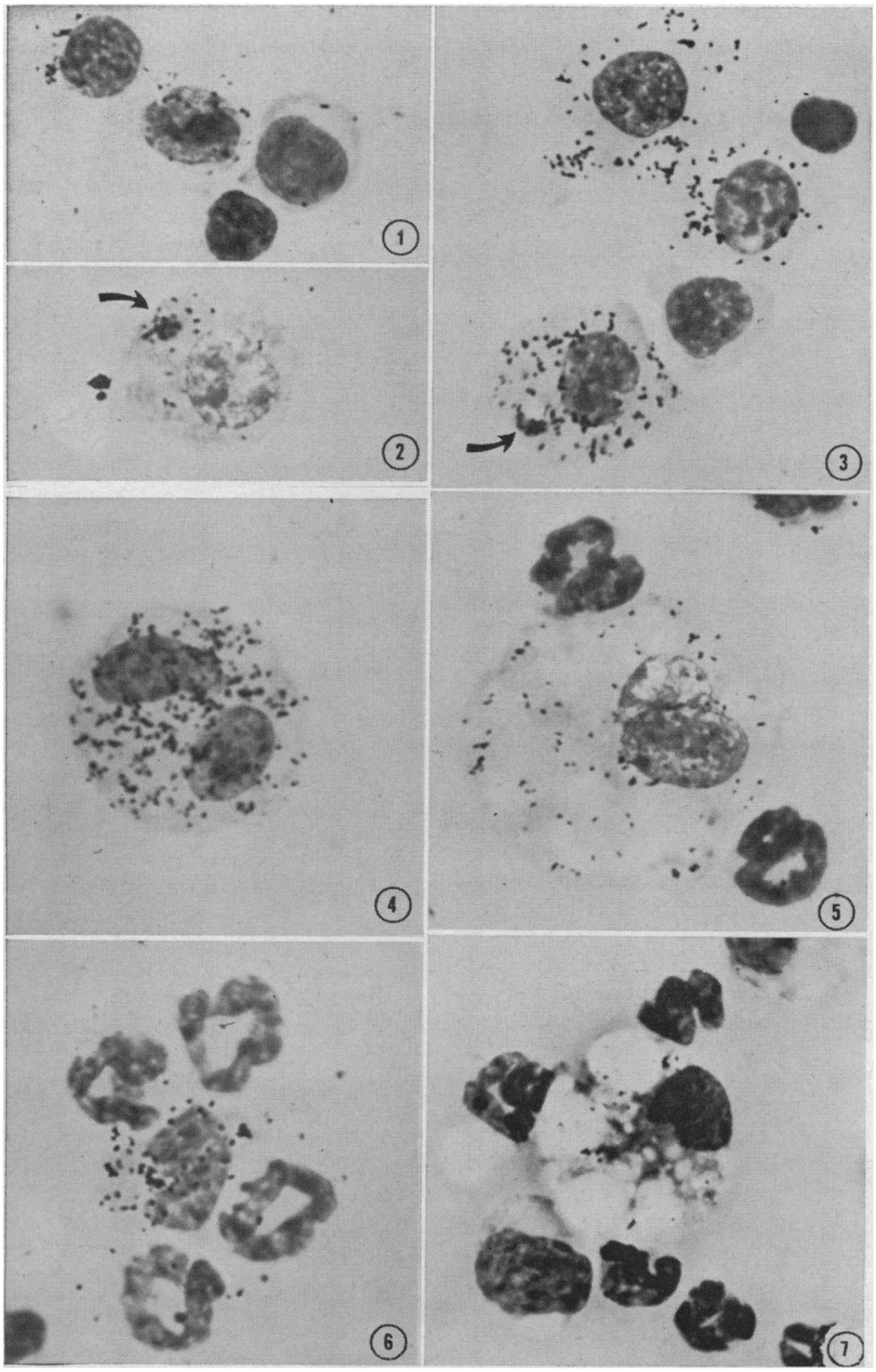

Figs. 1–7. Autoradiograms of inflammatory cells taken from the peritoneal fluid of mice at various times after injection of tritiated tetanus toxin. Fig. 1. Labeled lymphocytes 10 days after injection. Figs. 2 and 3. Labeled macrophages 10 days after injection. The radioactive material is often associated with basophilic material in the cytoplasm (see arrows). Fig. 4. Highly labeled binucleated cell from the inflammatory exudate produced by injection of diphtheria toxoid 30 days after injection of radioactive tetanus toxin. Fig. 5. Highly labeled binucleated cell from an animal which had been rechallenged with tetanus toxoid 30 days after injection of radioactive tetanus toxin. This cell is highly vacuolated and two eosinophils appear to be attached to it. Fig. 6. Labeled disrupted macrophage and four attached eosinophils. This rosette is from a mouse rechallenged with tetanus toxoid 10 days after injection of radioactive tetanus toxin. Fig. 7. Labeled cell from an animal which had been rechallenged 270 days after injection of radioactive tetanus toxin. This highly vacuolated cell had three eosinophils attached.

of radioactivity in the inflammatory area (*4*). It would appear that the migration of these labeled cells into the inflammatory area initiates a series of reactions when the cells come in contact with specific antigen. The cells become swollen and release biologically active substances which produce a chemotactic response from the eosinophils (*2, 5*). The accumulation of vacuolated cells with associated eosinophils occurs before the formation of measurable serum antibody, and the time of antibody production corresponds to the time the eosinophils and the fragments of the hypersensitive cells are engulfed by macrophages (*6*). This suggests that these cellular reactions are part of the processes causing delayed hypersensitivity and the formation of antibody (*7*).

ROBERT S. SPEIRS
Department of Anatomy,
Downstate Medical Center, State
University of New York, Brooklyn 3

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Crystal Structures of Titanium, Zirconium, and Hafnium at High Pressures

Abstract. *At high pressures, as determined by x-ray analysis, titanium and zirconium metal have a distorted, body-centered-cubic structure. This phase persists on pressure release. The normal hexagonal close-packed structures are recovered when the metals are heated. An electronic shift must occur in the transition. Hafnium metal showed no such transition.*

The isoelectronic transition elements $[nd^2(n+1)s^2]$ titanium, zirconium, and hafnium are all hexagonal closed-packed (h.c.p.) metals at room temperature and pressure, while at high temperatures they adopt a body-centered-cubic (b.c.c.)

Table 1. Omega phases of titanium and zirconium at atmospheric pressure.

Phase	Ti	Zr
c	2.813 Å	3.109 Å
a	4.625 Å	5.036 Å
c/a	0.608	0.617
$\rho(\omega)$	4.581	6.657
ρ(h.c.p.)	4.503	6.505

Table 2. Interatomic distances and number of neighbors in the omega and h.c.p. phases.

Distances and neighbors	Distance (Å)	
	Ti	Zr
$d_1(2)$	2.813	3.109
$d_2(12)$ (6)	3.018	3.297
$d_3(3)$	2.670	2.908
$d_4(6)$	2.950	3.232
$d_5(6)$	2.897	3.179
$R(1)$	1.324	1.454

structure (*1*). From volume measurements Bridgman reported a possible transition in titanium (*2*) at about 35,000 kg/cm^2 but he did not observe effects in its electrical resistance (*3*). In a different set of volume measurements (*4*), he reported no transition in titanium or zirconium, although the data were somewhat anomalous for titanium. Electrical resistance measurements (*3*) showed a transition in zirconium at 80,000 kg/cm^2 (which should be corrected to about 60,000 kg/cm^2). Young *et al.* (*5*) noted the zirconium transition and that the b.c.c. forms were denser. They suggested that the zirconium transition was h.c.p.↔b.c.c. and that titanium and hafnium (also yttrium) might possibly transform between 90 and 130 kb and hence be useful for pressure calibrations. Thermodynamic data of Kaufman (*6*), together with known volume data (*1*), may be used to estimate roughly that the transformation from h.c.p. to b.c.c. occurs at much higher pressure than the 60,000 kg/cm^2 reported for zirconium by Bridgman. I decided to investigate these three elements by a high-pressure x-ray technique (*7*) .

All three metals were studied in two ranges of purity (*8*) but no discernible differences in behavior between batches were found. Samples of each metal (diluted appropriately with boron to minimize absorption) were x-rayed at high pressures. Titanium and zirconium showed diffraction patterns characteristic of a new structure. Hafnium did not. On release of pressure the new structures for titanium and zirconium quenched (persisted at one atmosphere). Hence undiluted samples of titanium and zirconium were x-rayed after exposure to pressure. Powder patterns taken with filtered Mo radiation (the forced admixing of boron with the samples obscured patterns taken with filtered Cu radiation) were indexed hexagonal with the crystallographic parameters given in Table 1. The intensities (and c/a ratios) for the new phases of titanium and zirconium were appropriate for the ω phase found in titanium-vanadium alloys by Silcock *et al.* (*9*) and Bagaryatskii *et al.* (*10*), and the same structure found in zirconium-vanadium and zirconium-niobium alloys by Hatt and Roberts (*11*). This is a distortion of the b.c.c. structure to a hexagonal structure. As such, it is much more open-packed than hexagonal close-packed, and a shift in electronic levels leading to a smaller atomic size must have occurred. Such a transition was reported recently for Ytterbium by Hall *et al.* (*12*) and the type was predicted earlier by Jamieson and Lawson (*13*). A similar shift must occur at the high-temperature h.c.p.↔b.c.c. transitions for the b.c.c. form to be denser.

When the ω forms of titanium and zirconium were heated at 110°C for 17 hours a complete conversion to h.c.p. took place in the former and there was no change in the latter. Four hours at 195°C were sufficient to alter partially ω zirconium to h.c.p. Since both pressure transitions are monotropic the true equilibrium pressures are unknown.

Some estimate of the electronic changes that occur when titanium and zirconium adopt the ω structure may be made by a consideration of interatomic distances. The lattice points are (0,0,0,), (⅔, ⅓, ½), and (⅓, ⅔, ½). The (0,0,0,) points have two atoms at $d_1 = c$ and 12 atoms at

$$d_2 = a\,[1/3 + 1/4\,(c/a^2]^{\frac{1}{2}}$$

while the other two sites have three (coplanar) atoms at $d_3 = a/(3)^{\frac{1}{2}}$, two at d_1 and six at d_2. These distances are tabulated in Table 2 (for 1 bar pressure) together with d_4, the spacing perpendicular to c and d_5 (for the remaining six neighbors in twelve coordination) for the h.c.p. phase. The latter values and h.c.p. densities have been obtained or calculated from the data of Swanson *et al.* (*14*).

An interesting fact emerges. The closest approach in the structure is the three-coordinated d_3. Pauling (*15*) gives a formula

$$R(1) - R(n) = 0.3 \log_{10} n$$

for the change in atomic radii with change in coordination number N, $n = v/N$, where v is the "valence" and $R(1)$ is the "univalent radius" of the atom in question. Half of d_3 is almost exactly $R(1)$ as shown in Table 2 (from Pauling) for both elements. This can occur if $v = N$, that is, the valence of both elements in the omega phase becomes three. This could be achieved if one electron adopts a "strictly" localized *d*-state at each atom and leaves only three electrons to form a true conduction band. This suggestion also receives some support from the formation of the ω phase (*9–11*) in Ti and Zr alloys with V and Nb, elements which would otherwise increase the electron-to-atom ratio. It should be possible to observe this localized *d*-state in magnetic studies of these elements in this form.

JOHN C. JAMIESON

Department of the Geophysical
Sciences, University of Chicago,
Chicago 37, Illinois

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