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Letters to the Editor

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A Low Temperature Transformation in Lithium*

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LITHIUM has been reported as having a body-centered cubic structure in the range from ordinary temperatures to liquid air temperature.[1, 2] X-ray diffraction at low temperatures now reveals, however, that a transformation can be induced in the metal if it is plastically deformed at temperatures in the vicinity of −196°C.

Analysis of the Geiger-counter spectrometer record of the diffraction pattern shows that the new phase produced by this treatment is face-centered cubic in structure with the lattice constant $a_0=4.41\text{A}$ at −196°C. The body-centered cubic phase in the same sample at this temperature has $a_0=3.50\text{A}$. There is an expansion of atomic radius accompanying the increase of coordination number from 8 to 12, as would be expected, and because this expansion has the value 2.8 percent it follows that the calculated densities of the two phases are identical within experimental error. The calculated density is 0.534.

The transformation to the face-centered cubic form is accompanied by a series of audible clicks, as in the twinning of tin or magnesium and the formation of martensite. By analogy with these processes it may be concluded that the transformation goes by abrupt shear movement in small isolated regions. The constraints imposed by the material around these transforming regions can account for the fact that we have been unable to transform much more than half of any of the polycrystalline samples by any type of straining we have tried. Presumably then, proper straining of a single crystal might lead to complete transformation. The face-centered phase disappears fairly rapidly when heated above about −117°C.

We were led to search for low temperature transformations in various metals by C. Zener's theory of the susceptibility of body-centered cubic phases to instability at low temperatures,[3, 4] which may be summarized as follows. A homogeneous shear of 0.35 in a body-centered cubic structure along the (110) plane and the $[1\bar{1}0]$ direction will produce an atomic arrangement that is very nearly face-centered cubic. Consider the relative free energy of the two phases. The free energy of the body-centered cubic phase increases as the temperature is lowered, and increases more rapidly than would the free energy of a face-centered cubic phase, provided the thermal vibrations of the atoms in some direction of the body-centered structure are abnormally large. In metals and alloys of body-centered cubic structure that have filled inner shells of electrons, the shear constant $(C_{11}-C_{12})/2$ should be small and is, in fact, very small; as this constant applies to shear in the (110) plane in the $[1\bar{1}0]$ direction, the thermal vibration amplitudes in this direction should be large, and since the entropy is proportional to the logarithm of the amplitude it follows then that the entropy should be large. The free energy of a phase with large entropy rapidly increases as the temperature is lowered, since $F=U-TS$ and $\partial F/\partial T=-S$, where F is the free energy, U the internal energy, T the temperature, and S the entropy; it is not unlikely that F for the body-centered phase in such cases will exceed that for the face-centered phase and make a transformation possible, as in some compositions of beta-brass, where $(C_{11}-C_{12})/2$ is twice as large in the face-centered form as in the body-centered. Such transformations should be aided by shear in the direction for which the shear modulus is low, both because it reduces the sluggishness of the transformation by aiding the atoms in surmounting the potential barrier in this direction and because this is the direction required for the shear movement of the transformation.

A more detailed account of the investigation of this metal and others will be published elsewhere.

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[1] F. Simon and E. Vohsen, Zeits. f. physik. Chemie **133**, 165–187 (1928).

[2] E. Posnjak, J. Phys. Chem. **32**, 354–359 (1928).

[3] C. Zener, Phys. Rev. **71**, 846 (1947).

[4] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, to be published).

On the Hyperfine Structure of the Ground State of H and D Atoms

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RECENTLY[1] measurements of the hyperfine structure of H and D atoms have been carried out which are extremely interesting from a theoretical as well as an experimental point of view.

According to the latest precision measurements, not only the absolute values of the hyperfine structure splittings ν_H, ν_D differ from the theoretical value by about one part in 400, but also the ratio of these quantities differs from the theoretical value by about 1 part in 1700, the calculated value always being smaller than the observed. The theoretical evaluation was carried out with the aid of the well-known Fermi formula

$$\nu=\frac{8\pi}{3h}\frac{2I+1}{I}\mu_N\mu_0|\psi(0)|^2, \tag{1}$$

in which the nuclear spin is denoted by I; μ_N is the magnetic moment of the nucleus, μ_0 is Bohr's magneton, and $\psi(0)$ the Schroedinger wave function at the origin. Through $|\psi(0)|^2$, the Bohr radius of the ground state enters into