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 $a_0=4.41A$ at $-196°C$. The body-centered cubic phase in the same sample at this temperature has $a_0=3.50A$. 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 the expression of the hyperfine structure splitting, $|\psi(0)|^2$ being proportional to a^{-3}. It is customary to eliminate the Bohr radius by introducing the Rydberg constant for infinite mass, together with the reduced mass of the electron. It then turns out that the hyperfine structure splitting is given by the expression

$$\nu = C\frac{2I+1}{I}\mu_N\left(\frac{m_r}{m_0}\right)^3. \qquad (2)$$

Here C contains universal constants and numbers, while m_r stands for the reduced mass of H or D, respectively. m_0 denotes the electronic mass. The ratio ν_H/ν_D is then given by

$$\nu_H/\nu_D = (4/3)(\mu_H/\mu_D)(m_H/m_D)^3,$$

and the numerical value for ν_H/ν_D as observed, is 4.3416 compared with a computed value of 4.3393.

Equation (1) is derived by neglecting the small components of the Dirac equation and replacing the large components by Schroedinger functions.

The discrepancy observed which, if the accuracy of observation is sufficient, in the case of the ratio at least, cannot be ascribed to inaccurate values of the universal constants, makes it advisable to re-examine the derivation of (1).

We have obtained a value for ν by consistently using Dirac's equation, retaining all four components through the perturbation calculation and using the rigorous Dirac functions in the evaluation of the matrix element for the perturbed energy. The hyperfine structure splitting apart from numerical factors is now given by

$$\nu = C'\frac{e\mu_N}{(h/mc)^2}[1-(E/mc^2)^2]^{\frac{3}{2}} = C'\frac{e\mu_N}{(h/mc)^2}(2R/mc^2)^{\frac{3}{2}}. \qquad (3)$$

The second equation in (3) is obtained by the somewhat arbitrary insertion of the empirical Rydberg constant in place of R_∞ which would, of course, follow from the Dirac equation.

This calculation leads, within the accuracy aimed at, to the same value as given by (2), with the one difference that the ratio of reduced to electronic mass appears in the three-halves rather than in the third power. This correction diminishes the discrepancies between the observed and calculated values of ν_H and ν_D, as follows. For H, the discrepancy is reduced to one part in 600; for D, to one part in 500; both deviations are obviously still large if one believes in the presently accepted values of the universal constants.

The ratio ν_H/ν_D, on the other hand, now differs from its calculated value by only one part in 8000; this is much smaller than the accuracy claimed for the earlier determinations of μ_H/μ_D, which enters as a factor into (3) and is assumed to be known to about 1 part in 3000.

In interpreting this result, several points must be kept in mind: The accuracy of the experimental determination of μ_H/μ_D and the calculated value which contains it as its most uncertain element, are not yet sufficiently good to exclude a different dependence on the ratio of the reduced masses.

The theory here used is obviously not consistent; we have carried out all calculations with the one-body Dirac equation and taken into account the two-body nature of the problem by the empirical introduction of R_H and R_D. This point will need further theoretical study.

We have also investigated the question of how the electronic magnetic moment may be expected to depend on the nuclear mass and have found different results depending on the physical interpretation given to the coordinates which enter into the Dirac equation.

A detailed paper will follow shortly.

[1] J. E. Nafe, E. B. Nelson, and I. I. Rabi, Phys. Rev. 71, 914 (1947). I am greatly indebted to the authors for telling me about their results before publication.

Nuclear Capture of Mesons and the Meson Decay

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THE experiment of Conversi, Pancini, and Piccioni[1] indicates that the probability of capture of a meson by nuclei is much smaller than would be expected on the basis of the Yukawa theory.[2,3] Gamow[4] has suggested that the nuclear forces are due exclusively to the exchange of neutral mesons, the processes involving charged mesons and the β-processes having probabilities which are smaller by a factor of about 10^{12}.

We notice that the probability ($\sim 10^6$ sec.$^{-1}$) of capture of a bound negative meson is of the order of the probability of ordinary K-capture processes, when allowance is made for the difference in the disintegration energy and the difference in the volumes of the K-shell and of the meson orbit. We assume that this is significant and wish to discuss the possibility of a fundamental analogy between β-processes and processes of emission or absorption of charged mesons.

An immediate consequence of the experiments of the Rome group[1] is that the usual interpretation of the β-process as a "two-step" process ("probable" production of virtual meson and subsequent β-decay of the meson) completely loses its validity, since it would predict too long β-lifetimes: the meson is no longer the particle responsible for nuclear β-processes, which are to be described according to the original Fermi picture (without mesons). Consequently there is no need to assume that charged mesons have integral spin, as the Yukawa explanation of β-processes required. Once we believe that the ordinary β-process is not connected in any way with the meson, it is difficult to see strong reasons for the usual assumption that the meson decays with emission of a β-particle and a neutrino. We shall consider then the hypothesis that the meson has spin $\frac{1}{2}\hbar$ and that its instability is not a β-process, in the sense that it does not involve the emission of one neutrino. The meson decay must then be described in a different way: it might consist of the emission of an electron and a photon or of an electron and 2 neutrinos[5] or some other process.