On the Possibility of a Metallic Modification of Hydrogen

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Additional information on J. Chem. Phys.

	H₂	HD	D₂	ρ″: H₂−HD	
				Obs.	Theory
ω_e	4405.30	3817.09	3117.05	0.86648	0.86616
$x\omega_e$	125.325	94.958	63.034	0.7577	0.7502
$y\omega_e$	1.9473	1.4569	0.74526	0.748	0.650
$z\omega_e$	0.11265	0.07665	0.031573	0.680	0.563

calculating these constants.* The molecular constants of D₂ given in the table are the average values calculated from those of H₂ and HD, assuming the theoretical relationships between the reduced masses of H₂ and D₂ and of HD and D₂ to hold. The value of ΔG_1 (D₂) calculated by use of these constants is 2993.2 cm⁻¹, which differs from the experimental value of 2993.5 cm⁻¹ by only 0.1 cm⁻¹ more than the estimated accuracy of the experimental value. The agreement of the observed positions of the rotational vibration lines of the three isotopic molecules and the positions calculated from the new constants is very good, as may be seen from Table II.

The measurement of the heights of the intensity maxima of the microphotometer curves of

* It seems improbable that the theoretical relationships between the constants of the isotopic molecules could hold exactly due to differences to be expected in the potential energy curves from the differences in the electronic zero-point energies of the hydrogen and deuterium atoms as well as the molecules. This effect, however, should be small and not detectable in the constants in Table III.

Plates I and II shows an alternation of intensities of the pure rotational lines of D₂, the lines involving transitions from even states being more intense. This, in agreement with previous work on emission spectra,[12, 13] allows one to conclude that the deuterium nucleus obeys the Einstein-Bose statistics and has a spin different from zero. The semi-quantitative measurements agree very well with those expected according to Placzek's theory[14] if Murphy and Johnston's value of the spin equal to 1 is used. Though the theory predicts the absence of lines corresponding to V : 0–1, J : 0–0 transitions a line for this transition for HD was observed on Plate III.

ACKNOWLEDGMENT

[12] G. N. Lewis and M. F. Ashley, Phys. Rev. 43, 837 (1933).
[13] G. M. Murphy and H. Johnston, Phys. Rev. 46, 95 (1934).
[14] G. Placzek, Handbuch der Radiologie VI (1934), Vol. 2, p. 343.

On the Possibility of a Metallic Modification of Hydrogen

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Any lattice in which the hydrogen atoms would be translationally identical (Bravais lattice) would have metallic properties. In the present paper the energy of a body-centered lattice of hydrogen is calculated as a function of the lattice constant. This energy is shown to assume its minimum value for a lattice constant which corresponds to a density many times higher than that of the ordinary, molecular lattice of solid hydrogen. This minimum—though negative—is much higher than that of the molecular form. The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.

(1) INTRODUCTION

THE present calculation of the constants of metallic hydrogen has a threefold purpose. First, we wanted to explore the possibility of preparing metallic hydrogen under high pressures.[1] The hope for this, however, appears to be small, as the pressures under which metallic hydrogen would be stable seem to be unattainable with the present techniques. Second, it seemed to us important to check the free electron method of calculating wave functions and heats of vaporization[2] in a case where experiments give an upper limit to the energy. The obvious instability of metallic hydrogen under ordinary pressure shows that its heat of formation is smaller than that of the molecular hydrogen. This condition proved to be only too well fulfilled. Finally, we hoped to obtain some information concerning the conditions for the metallic state and the line separating metals from metalloids in the periodic table.[3] This purpose has been achieved by the present work to the extent expected, but this point, although perhaps apparent to the reader, will not be stressed in the present paper.

(2) CALCULATION

The calculation itself was a rather mechanical application of the principles outlined elsewhere.[2] First, the energy $E(r_s)$ was found for which the solution of the Schrödinger equation with the ordinary Coulombic potential $-e^2/r$ had zero derivative at distance r_s. This was done by a numerical method and, in addition, checked by an analytic approximation,[4] which gave a direct

expression for the wave function needed for subsequent work. The plot (lower curve of Fig. 1) shows the results of the numerical method which gave the more accurate results. Its values lie about 0.02 Ry (Rydberg units) below those of the analytic formula. In this case $E(r_s)$ has no minimum, as in case of Na, but instead continues to fall to $-\infty$ for $r_s \rightarrow 0$. In Na the rising of $E(r_s)$ for small r_s results from the energy necessary to press the valence electron into the inner shells, whereas no such shell exists for hydrogen.

The upper curve of Fig. 1 is obtained by adding to $E(r_s)$ the Fermi energy for free electrons,

$$(2.2099/r_s^2)\,\mathrm{Ry},$$

where r_s is expressed in Bohr units $\hbar^2/e^2m$. This corresponds to the calculation adopted in ref. 2 I and gives a minimum of $E = -1.156$ for $r_s = 1.50$. This would give a density of 0.80 (as compared to 0.087 in the solid molecular form!) and a heat of vaporization of 48.7 cal. into atomic hydrogen, as compared with 52.5 cal., the heat of formation of the molecular form. We see that the molecular form is the more stable, even according to this very approximate calculation, but if this were all, it would probably still be possible to transform it under pressure to a metallic form.

Unfortunately, a great number of corrections must be applied to the simple picture given in ref. 2 I which decreases the stability of the metallic form in this instance. These corrections are given for the flat wave functions in refs. 2 II and 2 III. They are:

[1] It was J. D. Bernal who first put forward the view that all substances go over under very high pressures into metallic or valence lattices.

[2] (I) E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); (II) **46**, 509, 1934; (III) E. Wigner, ibid. **46**, 1002 (1934); (IV) F. Seitz, ibid. **47**, 400 (1935); (V) J. C. Slater, ibid. **45**, 794 (1934). E. L. Hill remarks in a "Note on the Statistics of Electron Interaction" (Physik. Zeits. Sowjetunion **7**, 447 (1935)) that the expressions "parallel spin" and "antiparallel spin" should be replaced by "parallel spin Z components" and "antiparallel spin Z components," respectively. The former expressions are not quite equivalent with the latter ones according to the general formalism of the statistical interpretation of quantum mechanics and can be used only as an abbreviation for them. (This is done in the present paper also.) We believe that Dr. Hill's further remarks concerning the papers of this reference are based on a misunderstanding.

[3] Interesting quantum-mechanical considerations on this point have been put forward by F. Hund (International Conference on Physics, October 1934, London).
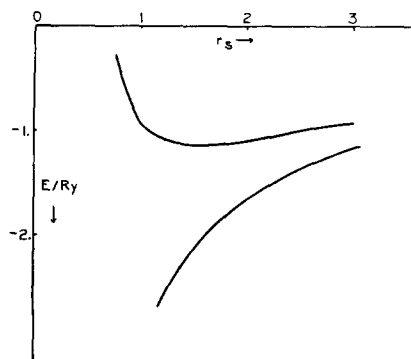
[4] To be given in Section 3.

FIG. 1. Lower curve—the energy of the electrons without momentum, the upper curve—total energy as a function of lattice constant. Both according to a naïve free electron theory.

(a) The difference between the energy of the electron clouds (§2 in II) and the exchange energy (§3 in II)

$$0.284/r_s - 0.017/r_s^2(E_k - E), \quad \text{(in Rydberg units),} \quad (1)$$

where E_K is a mean value of the energy of the higher s terms and has been estimated[4] to be about $20 \text{ Ry}/r_s^2$. The second term in (1) is, therefore, almost negligible.

(b) The correlation energy, calculated in ref. 2 III, which can be represented for $r_s > 1$ rather closely by

$$-0.584/(r_s + 5.1). \quad (2)$$

(c) A correction for the Madelung number will be added in the next section.

The energy after the corrections (a) and (b) have been added is plotted on a magnified scale on the lowest curve in Fig. 3. One sees that a great part of the binding energy is lost.

(3)

It is very probable that the wave functions have nearly the form $e^{ip \cdot x/h}$, not only in Na, but also in the other alkalies excepting Li.[5] In H this is not the case, however, and there will be further corrections introduced into the energy curve similar to those calculated for Li by F. Seitz.[2 IV] Still the situation for H is rather different from that for Li. In H the wave function of the lowest energy electron ($p = 0$) is strongly modulated but the modulation does not increase much for higher p functions. In Li the wave function for $p = 0$ was quite flat and the modulation increased with increasing p.

For the calculation of these effects an approximate method has been used. The equation for the wave function of the electron with momentum p, multiplied by $e^{ip \cdot x/h}$, is[6]

$$H_\mu \chi_\mu = -\Delta\chi_\mu - i\mu \cdot \text{grad } \chi_\mu - 2\chi_\mu/r = \epsilon_\mu \chi_\mu,$$
$$\mu = 2\hbar p/e^2 m. \quad (3)$$

Here the ϵ_μ does not include the kinetic energy of the flat wave functions, $p^2/2m = \mu^2/4$ Ry. The $\epsilon_\mu - \epsilon_0$ will give us the change in the Fermi energy, and the wave functions χ_μ the change in charge distribution, which are both caused by the fact that the electrons are not free in the lattice. The charge distribution is used in a

[5] Cf. F. Mott and C. Zener, Proc. Camb. Phil. Soc. **30**, 249 (1934); also J. Bardeen and E. Wigner, Phys. Rev. **48**, 84 (1935); for Li see reference 2 (IV) and J. Millman, ibid. **47**, 286 (1935).

[6] Cf. Eq. (11), reference 2 (II). The energy in (3) is in Rydberg units Ry and the length in Bohr units.

recalculation of the interaction of the electron clouds and the Fermi hole (exchange energy). We shall see that χ_μ can be assumed to be the sum of a function of r alone (s part) and a function of r multiplied by $(\mu \cdot r)$ (p part). The boundary condition for the χ_μ is periodicity in the lattice, which means zero derivative for the s part, and vanishing of the p part on the surface of the s sphere.

Eq. (3) has been solved by a perturbation method. We shall need only those solutions of the unperturbed equation

$$-\Delta\xi_{nl} = \eta_{nl}\xi_{nl}, \quad (4)$$

which are functions of r alone ($l = 0$, or the s part of χ), and those which are functions of r multiplied by $(\mu \cdot r)$, ($l = 1$ or the p part of χ). The boundary conditions for these ξ functions are the same as for the corresponding part of χ. We have[2 II]

$$\xi_{00} = (3/4\pi r_s^3)^{\frac{1}{2}}, \quad \xi_{n0} = c_n(\sin \omega_n r)/r,$$
$$\xi_{n1} = (3^{\frac{1}{2}}c_n/\mu\omega_n)(\mu \text{ grad})(\sin \omega_n r)/r, \quad (5)$$
$$\eta_{00} = 0, \quad \eta_{n0} = \eta_{n1} = \omega_n^2,$$

with
$$\omega_1 = \frac{1.430\pi}{r_s}, \quad c_1 = \frac{1.024}{(2\pi r_s)^{\frac{1}{2}}};$$
$$\omega_n = (n + \tfrac{1}{2})\frac{\pi}{r_s}, \quad c_n = \frac{1}{(2\pi r_s)^{\frac{1}{2}}}$$

when the last two expressions hold well for $n > 1$ only.

Next we must calculate the matrix elements of H_μ. All terms give nonvanishing elements between ξ_{nl} and $\xi_{n'l}$ only, except for $i\mu \cdot \text{grad}$ which gives elements between ξ_{nl} and $\xi_{n'l+1}$. We have

$$(H_\mu)_{00; \, 00} = -3/r_s;$$
$$(H_\mu)_{10; \, 10} = 20.2/r_s^2 - 5.65/r_s;$$
$$(H_\mu)_{n0; \, n0} \approx (H_\mu)_{n1; \, n1} \approx (n + \tfrac{1}{2})^2\pi^2/r_s^2;$$
$$(H_\mu)_{11; \, 11} = 20.2/r_s^2 - 3.66/r_s; \quad (6)$$
$$(H_\mu)_{n'0; \, n1} = -(i\mu\omega_n/3^{\frac{1}{2}})\delta_{n'n};$$
$$(H_\mu)_{00; \, 10} = 1.36/r_s;$$
$$(H_\mu)_{00; \, n0} = 2(6)^{\frac{1}{2}}/(n + \tfrac{1}{2})\pi r_s.$$

For $\mu = 0$, this gives, by Rayleigh-Schrödinger formulas,

$$\epsilon_0 = -\frac{3}{r_s} - \frac{(1.36)^2}{20.2 - 2.65r_s} - \sum_{n=2}^{\infty} \frac{24}{(n+\frac{1}{2})^4 \pi^4},$$
$$\chi_0 = \xi_{00} + \frac{1.36r_s}{20.2 - 2.65r_s}\xi_{10} + \sum_{n=2}^{\infty} \frac{2(6)^{\frac{1}{2}}r_s}{(n+\frac{1}{2})^3 \pi^3}\xi_{n0}.$$

(7)

These are the formulae to which we referred in Section 2. For $\mu \neq 0$, we diagonalized the three rows and columns of H_μ referring to ξ_{00}, ξ_{10} and ξ_{11} and used only for the remaining ones the Rayleigh-Schrödinger method. This was advisable, because $(H_\mu)_{10;\ 10}$ and $(H_\mu)_{11;\ 11}$ were close together. This gave

$$\epsilon_\mu = -\frac{3}{r_s} - \frac{1.85}{20.2 - 2.65r_s - 6.72\mu^2(20.2 - 0.6r_s)^{-1}} \\ -0.0093. \quad (8)$$

The mean value of $\epsilon_\mu - \epsilon_0$ with the weight μ^2, from $\mu = 0$ to $\mu = 3.84/r_s$ is the correction to the Fermi energy; it is plotted in the lowest curve of Fig. 2. It is negative, just as in Li, because there is no p level below the s level of the valence electron. The energy $\epsilon_\mu - \epsilon_0$ is no longer very accurately proportional to μ^2, because the effect of the next Brillouin zone is appreciable.

(4)

Next the interaction of the electron cloud and the more accurate exchange energy must be derived. The greater density near the nucleus makes it evident that the first will be greater than the free electron value assumed in the previous section. This is true also for the exchange energy, because the Fermi hole is more effective in consequence of the uneven charge distribution. The two effects work against each other, but in contrast to Li, the former is greater here and decreases the binding.

The calculation of these quantities is a little laborious and contains nothing of principal interest. It will be sketched only.

The square of the calculated wave function, i.e., the electric density ρ, was approximated by an analytical expression[7] containing a constant

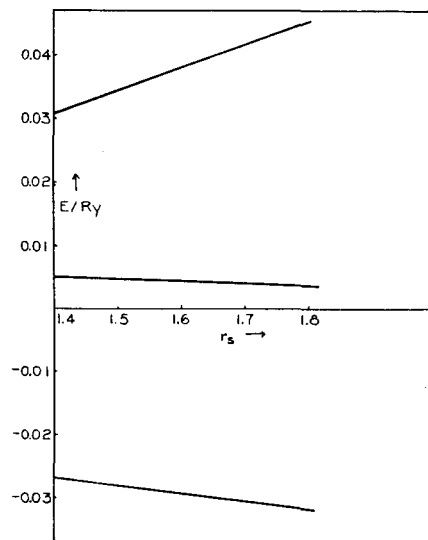[7] The reason for this is that only for this form were we able to perform the integrations.

FIG. 2. Bottom line, correction to the Fermi energy; middle line, correction for the Madelung number; top line, correction for the interaction energy.

and an exponentially decreasing charge distribution around each ion:

$$\rho = \rho_1 + \rho_2, \quad \rho_1 = e(1-c)/(4\pi r_s^3/3). \quad (9)$$

ρ_2 itself contains two parts: first the exponential charge distribution around the ion, in the s sphere in which we are, and second the exponential charge distribution around the other ions. The latter was averaged over all directions so that ρ_2 also became spherically symmetric in each s sphere

$$\rho_2 = \frac{ec\beta^3}{8\pi}\left[e^{-\beta r} + 4k\frac{Sh(\beta r)}{\beta r}\right], \\ k = e^{-2\beta r_s}(1 + \beta r_s + \beta^2 r_s^2/2)(\beta r_s - 1)^{-1}. \quad (9a)$$

The two constants c and β were adjusted so as to fit the square of the calculated wave function (7) best.

The potential corresponding to this charge distribution contains also two parts: Φ_1, corresponding to the constant part ρ_1 and Φ_2 corresponding to ρ_2 which could be easily calculated, and hence also the interaction of the electron clouds.

For the calculation of the exchange energy the wave functions of the electrons with momentum p were assumed to be in the form $e^{i(p \cdot x)/\hbar} \chi(r)$ where $\chi(r)$ is the wave function of the lowest state. Under these conditions, the exchange energy is[2 II, 2 III]

$$-\frac{e^2}{2} \int \rho(r)\rho(r')g(|r-r'|)\frac{1}{|r-r'|}drdr', \quad (10)$$

where

$$g(r) = 9\left[\frac{\sin (r/d) - (r/d) \cos (r/d)}{(r/d)^3}\right]^2$$

$$\approx e^{-1.6r/d}\left[1 + 1.6\left(\frac{r}{d}\right) + 1.2\left(\frac{r}{d}\right)^2\right] \quad (10a)$$

with $d = 0.521r_s$. All the integrations could be carried out in elliptic coordinates. The result is evidently a quadratic function in c. The constant term is simply the exchange energy for flat wave functions $(c=0)$, i.e., $0.916 \text{Ry}/r_s$. The linear terms vanish as may be seen from the following. The integral of the first term in $\rho_1(r)$ times $g(|r-r'|)/|r-r'|$ over r is independent of r'. The product of this quantity and the terms containing c in $\rho(r')$, integrated over r', must vanish, since the integral of $\rho(r')$ is independent of c. By analogy the other linear term vanishes also and the sole remaining correction to the exchange energy of $0.916 \text{Ry}/r_s$ goes with c^2. Hence this is a second order effect[8] of the deviation from flatness of the wave function (9), and smaller than the increase of the interaction of the charge clouds which is a first order effect.

Next the change of the correlation energy, due to the uneven charge distribution, has to be considered. In the case of even distribution, the correlation energy is certainly smaller than $0.292e^2/r_s$, even for a very great lattice constant. For the actual uneven distribution in a greatly expanded lattice, however, this energy is as follows. Hartree's equations, solved for many electrons in the field of many ions, give as wave functions of the electrons a sum of spherically symmetric maxima around every ion. If all ions are sufficiently far removed from each other,

these waves—let their form be $u(r)$—no longer overlap. The total interaction energy per electron is

$$\frac{1}{2}\int \Phi(r)|u(r)|^2 4\pi r^2 dr \quad (11)$$

where $\Phi(r)$ is the potential of the charge distribution $|u(r)|^2$. Since no such interactions actually exist, Hartree's equation gives an incorrect result by this amount, which will be compensated by the exchange and correlation energy.

If Fock's picture is used instead, the interaction energy between electrons with parallel spins vanishes in consequence of the enormously increased Fermi hole. There remains still the interaction between electrons with antiparallel spin, by which amount Fock's picture is still in error. This remaining half of (11) must be nullified by the correlation energy. It follows that this energy must greatly exceed $0.292e^2/r_s$, the largest value possible for flat functions. We see that the correlation energy is increased by the modulation of the waves by a greater factor than the exchange energy, and it becomes in the limiting case of an infinite lattice just one-half of (11), approximately $\frac{1}{4}\text{Ry}$ per electron.[9]

We have increased the correlation energy for flat waves, given in,[2 III] by the same factor by which the exchange energy appeared to be increased. The total change of the electron interaction energy was positive, and plotted in Fig. 2 also.

Finally, the correction for the Madelung number, as given in appendix 2, Reference[2 II] is given in the same plot. The sum of all three corrections has been added to the curve of Fig. 3 and the upper full line of this figure obtained. This curve assumes its minimum of -1.05Ry (heat of vaporization about 16 Cal.) for $r_s = 1.63$ Bohr units, corresponding to a density of 0.62. The possible error in these figures is quite large, because the correction quantities are so great.

(5)

The last quantity which had to be calculated for the thermal constants of metallic H was the zero-point energy corresponding to the half-

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[8] This differs from the case for Li.

[9] We emphasize this point since doubts have been raised whether the correlation energy actually exists.
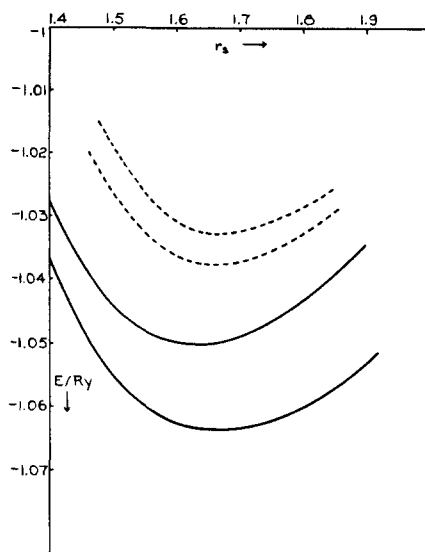
FIG. 3. Energy of the lattice as a function of lattice constant. Lowest curve, for flat wave functions; second curve with all corrections, except zero-point energy of nuclei; the dotted lines contain the zero-point energy, the lower for heavy, the upper for ordinary H.

quanta vibration of the nuclei. If the elastic constants of the medium were known, the elastic spectrum and the zero-point energy could be calculated following Blackman[10] or a paper of Barnes, Brattain, and Seitz.[11] Since, however, only the compressibility can be derived from Fig. 3 (and this only very inaccurately, as it may be in error by as great a factor as two), it was performed by the older method of Debye.[12]

From the curvature of the upper curve in Fig. 3 one obtains for the reciprocal compressibility of a lattice of very heavy hydrogen,

$$\tfrac{1}{3}(c_{11}+2c_{12}) = 2.9\times10^{12} \text{ dyne/cm}^2 \text{ for } r_s=1.5$$
$$= 1.5\times10^{12} \text{ dyne/cm}^2 \text{ for } r_s=1.6$$
$$= 1.1\times10^{12} \text{ dyne/cm}^2 \text{ for } r_s=1.7$$
$$= 0.8\times10^{12} \text{ dyne/cm}^2 \text{ for } r_s=1.8.$$

By analogy with other metals $c_{11}=2c_{12}=4c_{44}$ was assumed. The zero-point energy is then about

$0.0244(E'')^{\frac{1}{2}}$Ry, where E'' is the second derivative of the energy in Ry with regard to r_s in Bohr units. For the isotropic hydrogen with mass two the value is $0.0173(E'')^{\frac{1}{2}}$Ry. The dotted lines of Fig. 3 give the final results for the lattice energy, the upper one is for light, the lower for heavy hydrogen. The density of the former is 0.59, its heat of formation out of atomic hydrogen 10 Cal. We think that this figure is somewhat too low because the correlation energy is greater than we assumed it to be.

(6) CONCLUSION

The great density of the hypothetical metallic form of H is not surprising. It seems to be the general rule that the density of the metallic and valence lattice of a substance be greater than that of the layer lattice, and this in turn has greater density than the molecular lattice. Table I illustrates the point.

This table makes it natural to assume that all atoms are bound together by shared electron forces in metallic and valence lattices, and that this is the case also for the atoms within a layer in layer lattices. The different layers are bound together, however, more weakly, perhaps by van der Waals forces. This is well in accord with the general geometric considerations of A. Reis and K. Weissenberg.[13] It seems sensible, therefore, to speak about valence-like forces between two atoms in a lattice, if the density of the outermost electrons of both overlaps considerably at this distance.[14]

The heat of formation of the ordinary, molecular H_2 lattice is 52.5 Cal., practically one-half of the heat of dissociation. Although the figures of the preceding section may be in error by quite a few calories, it is evident that the molecular form is so much more stable (by about 40 Cal.) than the metallic, that the chances of obtaining the latter are extremely small.

In the ordinary lattice, there are two "nearest distances." The distance between two atoms of the same molecule is $0.75A=1.45a_0$, while the nearest distance between two H atoms of

[10] M. Blackman, Proc. Roy. Soc. London **A148**, 365, 384, (1935); **149**, 117, 126 (1935).
[11] Barnes, Brattain and Seitz, Phys. Rev. **48**, 582 (1935).
[12] Cf. e.g., E. Schrödinger, *Geiger-Scheel Handbuch der Physik*, Vol. X.

[13] A. Reis, Zeits. f. Physik **1**, 204 (1920); **2**, 57 (1920); K. Weissenberg, Zeits. f. Krist. **62**, 12, 52 (1925).
[14] This corresponds also to the ideas developed by L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); J. C. Slater, Phys. Rev. **38**, 1109 (1931).

TABLE I.

SUBSTANCE	DENSITY		DENSITY
As, metallic	5.72	yellow	2.03
Diamond	3.51	graphite	2.24
Black phosphorus	2.70	yellow	1.83
Se, metallic	4.82	red	4.47
Sn, white	7.28	grey	5.76

different H_2 molecules is about $3.3A = 6.3a_0$.[15] If one compresses the ordinary lattice, the latter distance will decrease, the former increase, as follows already from the calculations of F. London.[16] Thus, the increase of the pressure brings the intermolecular distances nearer to the intramolecular distances, and the lattice will become more similar to a simple lattice than it is at low pressures. It is possible that this goes on continually, and that one reaches a simple close packed lattice with metallic properties only in the limiting case of infinite pressures.

During the increase of pressure, the total energy of the substance will increase by the work done (we assume very low temperatures). It is possible, thus, that the energy of the continuously compressed lattice becomes at a certain volume, assumed at a very high pressure, greater than that of another modification. In this case there will be a *discontinuous change* to the latter.[17] Whether or not such a transition will occur into the metallic modification, depends on the magnitude of the compressibility of the molecular form at high pressures. The smaller this is, the greater will be the pressure necessary for a certain change in volume, and also the energy increase at this compression. If the extremely high

compressibility at ordinary pressures,[18] which is 2.10^{-9} cm^2/dyne, would hold throughout, the molecular form would be stable for all volumes. This is not possible, however, and the compressibility certainly decreases with increasing pressure, but one cannot tell, at present, whether it decreases sufficiently to make the metallic form stable at *any* pressure. One calculates easily, that even under the assumption of the most advantageous compressibility at high pressures, the pressure necessary for the transformation is 250,000 atmos., which is outside the scope of the present technique.

The objection comes up naturally that we have calculated the energy of a body-centered metallic lattice only, and that another metallic lattice may be much more stable. We feel that this objection is justified. Of course it is not to be expected that another simple lattice, like the face-centered one, have a much lower energy,— the energy differences between these forms are always very small. It is possible, however, that a layer-like lattice has a much greater heat of formation, and is obtainable under high pressure. This is suggested by the fact that in most cases of Table 1 of allotropic modifications, one of the lattices is layer-like,[19] the other either metallic, valence, or molecular. The difficulties for such an experiment will be greatly increased by the necessity of the formation of a nucleus for the new lattice.

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[15] The calculated nearest distance for the metallic form is 1.5A.

[16] F. London, Zeits. f. Elektrochemie **35**, 552 (1929); H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931).

[17] Such polymorphic transitions induced by pressure in solids are described by P. W. Bridgman, Rev. Mod. Phys. **7**, 1 (1935).

[18] Measured by A. Eucken for the liquid form, Ber. deutschen Phys. Ges. 4 (1916).

[19] Diamond is a valence lattice, but graphite is a layer lattice (A. W. Hull, Phys. Rev. **10**, 661 (1917)). Yellow arsenic and phosphorus are evidently molecular lattices, black phosphorus a layer lattice (R. Hultgren and B. E. Warren, Phys. Rev. **47**, 808 (1935)), and metallic As is also only approximately a simple lattice. The red, monoclinic selenium can be said to form a molecular lattice (F. Halla, F. Bosch, E. Mehl, Zeits. f. physik. Chemie **B11**, 455 (1930)), while the metallic modification is a thread lattice (A. J. Bradley, Phil. Mag. **48**, 477 (1924)). The situation seems to be most complicated with tin. Grey tin forms a diamond lattice, but shows otherwise no similarity to the valence lattice of diamond, while the metallic lattice has a rather complicated structure (H. Mark and M. Polanyi, Zeits. f. Physik **18**, 75 (1923)).