[CONTRIBUTION FROM THE DIVISION OF PHYSICAL METALLURGY, NAVAL RESEARCH LABORATORY]

ABSOLUTE COHESION IN METALS. DISRUPTIVE NEGATIVE PRESSURES AND CRITICAL DISRUPTIVE VOLUMES[1]

BY ROBERT FRANKLIN MEHL

RECEIVED AUGUST 16, 1929 PUBLISHED FEBRUARY 6, 1930

The work of A. F. Joffe[2] has served to demonstrate that the tensile strength of crystals of sodium chloride as measured in air may be very greatly increased by the solvent action of water operating on the crystals during the tensile test (from 0.44 kg./mm.^{2} to 160 kg./mm.^{2}) and that this higher tensile strength indeed approaches the theoretical tensile strength (200 kg./mm.^{2}) as calculated by Zwicky[3] by an extension of the Born lattice dynamics.

Zwicky's calculation was based on the "theory of heteropolar crystals as developed by Madelung, Kossel, Born and others." It gives a negative pressure exerted in one dimension only, that is, as in the case of two separating plane surfaces, and is in qualitative agreement for sodium chloride with the calculation performed by Polanyi[4] making use of values for surface energy computed by the use of the lattice theory of Born. Joffe[5] has carried out a somewhat similar calculation which yields a negative pressure exerted in three dimensions, a quantity which likewise may be taken as a measure of absolute cohesion. The calculation of this maximum negative pressure is carried out in the following way. Born's well-known lattice energy equation is

$$U = -\frac{A}{r^m} + \frac{B}{r^n} \qquad (1)$$

where U is the energy, A and B are constants, r is the interatomic distance defined as the cube root of the atomic volume divided by Avogadro's number. The first term represents the attractive potential and the second term the repulsive, with the condition that $n \gg m$. At the normal (zero external pressure) distance r_0, $\partial U/\partial r = 0$, that is, the force is zero. At any other distance we have

$$\frac{\partial U}{\partial r} = f = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}} \qquad (2)$$

The terms for attraction and repulsion, mA/r^{m+1}, and $-nB/r^{n+1}$, respectively, may be plotted against r, as Joffe has done.[6] This gives a

---

[1] Published by permission of the Navy Department, Washington, D. C.

[2] Summarized sufficiently for the present purpose in his book, "The Physics of Crystals," McGraw-Hill Book Company, New York, 1928.

[3] Zwicky, *Physik. Z.*, **24**, 131–137 (1923).

[4] Polanyi, *Z. Physik*, **1**, 323 (1921).

[5] Ref. 2, p. 21.

[6] Ref. 2, p. 16. The terms of potential in Equation 1 can be plotted in a similar way. It is to be noted, however, that Joffe's diagram for potentials is incorrect, since it shows the energy curve passing through zero at $r = r_0$, whereas at equilibrium the potential is not zero but a minimum.

set of curves similar to those given in Fig. 1, where $\pi/V^{n'}$ is to be compared with mA/r^{m+1} and $-\pi/V^m$ with $-nB/r^{n+1}$, and where V replaces r. Since we have the condition $n \gg m$, upon expansion (increasing r) the force reaches a maximum negative value and thereafter approaches the r-axis asymptotically. This maximum negative value of the force corresponds to a maximum possible expansion of the crystal, beyond which it will disrupt. Transferring into terms of pressures ($p = -\partial U/\partial V$; $\partial p/\partial V = -\partial^2 U/\partial V^2$) and making use of Equation 2 we may calculate the value of r at which the crystal will disrupt. Using this value the maximum negative pressure may be computed.[5] For sodium chloride this value is 350 kg./mm.[2]

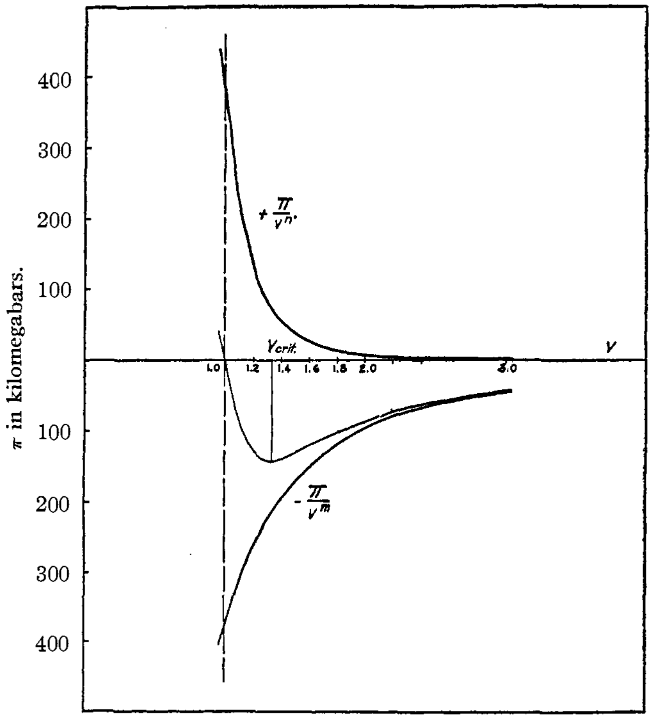

Fig. 1.—Internal pressure–volume curves for copper.

This method has not been applied with success to metals, largely because of difficulty with the exponents m and n, and also because of the uncertainty in the application to metals of the conceptions underlying Equation 1, which is intended to treat of point charges in definite and known positions. It is the purpose of this paper to point out that the negative pressures necessary for disruption—disruptive negative pressures—may be calculated from the equation of state for solids developed by the late T. W. Richards.[7]

$$p + \pi_0 \left(\frac{V_0}{V_1}\right)^m = \pi_{p_0} \left(\frac{V_0}{V_1}\right)^n + P_\theta \qquad (3)$$

in which p represent the external (atmospheric) pressure, $\pi_0(V_0/V_1)^m$ the internal cohesive pressure, $\pi_{p_0}(V_0/V_1)^n$ the internal expansive pressure, P_θ the internal expansive pressure caused by thermal agitation, V_0 the volume at p_0, and V_1 the volume at p_1. In this case also $n \gg m$.

For convenience in mathematical treatment this equation may be condensed[8] to

$$p + \pi_0 \left(\frac{V_0}{V_1}\right)^m = (\pi_{p_0} + P_\theta) \left(\frac{V_0}{V_1}\right)^{n'} \qquad (4)$$

With zero external pressure $\pi_0 = \pi_{p_0} + P_\theta$, since $V_0 = V_1$. π_0 and $\pi_{p_0} + P_\theta$ are thus constant and equal.

Rewriting (4) we have

$$p = -\pi_0 \left(\frac{V_0}{V_1}\right)^m + (\pi_{p_0} + P_\theta) \left(\frac{V_0}{V_1}\right)^{n'} \qquad (5)$$

Setting $V_0 = 1$ and $\pi_0 = (\pi_p + P_\theta) = \pi$, we have

$$p = -\frac{\pi}{V^m} + \frac{\pi}{V^{n'}} \qquad (6)$$

The condition that p passes through a maximum (negative) pressure, which Equation 6 demands, is $\partial p/\partial V = 0$. Differentiating (6) with respect to volume we may solve for V

$$V = V_{\text{critical}} = \left(\frac{n'}{m}\right)^{1/(n' - m)} \qquad (7)$$

This gives, then, the value for V at which the pressure passes through a maximum, in terms of the coefficients m and n, and is, therefore, the critical disruptive volume. In order to obtain the corresponding value for the disruptive negative pressure we may substitute this value in Equation 6 with the introduction of known values for m, n', π_0 and $\pi_{p_0} + P_\theta$, and solve for p, which may then be designated $p_{\text{max.}}$.

This formal treatment of Richards' equation of state, then, gives values for $p_{\text{max.}}$ and V_{critical} in a manner wholly analogous to the treatment of Born's equation as performed by Joffe. With the values of the coefficients m and n' and of the internal pressures calculated for the pure metals by Richards, it is, therefore, possible to obtain approximate values for the disruptive negative pressures and the critical disruptive volumes in metals.

It should be immediately remarked that both the method given here and that of Joffe can be regarded as only approximate because of the fact

---

[7] Richards' paper in *Chem. Rev.*, **2**, 315 (1925), is a good summary of his work and contains a complete bibliography, and together with his most recent paper on the subject, THIS JOURNAL, **48**, 3063 (1926), may be regarded as sufficient reference to the many papers he published in this field.

[8] Richards, *ibid.*, **48**, 3065 (1926).

that the constants in both cases are calculated from quantities measured at one atmosphere pressure or over a small range of pressures (up to only 10,000 kg./cm.^{2} in favorable cases). In addition, in the present case Equation 3 has been condensed into Equation 4, which may cause inaccuracies in higher ranges of pressures.[9] But admitting no great exactness in the final values, it is thought sufficiently interesting to make such calculations for the pure metals. At worst the present method suffers only those defects inherent in Joffe's method.

A comparison between the method proposed here and that given by Joffe may be carried out in the following way. π can be calculated for sodium chloride by the use of Richards' later and more accurate expression[10]

$$\pi = \frac{n'}{n' - m}\,\frac{R}{V_A\alpha_S} \tag{8}$$

where R is the gas constant, V_A the atomic volume, and α_S the volume coefficient of thermal expansion. Richards has not calculated the exponents m and n' for sodium chloride, but these may be borrowed from Born after suitable transformation.[11]

Taking $\boldsymbol{m} = 1$ and $\boldsymbol{n} = 9$, we find m to be 4/3 and n' 4. Using these calculated values for m and n' we can calculate the internal pressure π (which Richards designated π_0), as in Equation 3

$$\pi = \frac{n'}{n' - m}\,\frac{R}{V_A\alpha_S} = \frac{4}{4 - \frac{4}{3}} \times \frac{(83.16 \times 10^6)}{13.53 \times 115 \times 10^{-6}} \times 10^{-6} = 80{,}000 \text{ megabars}$$

---

[9] It should be noted in passing, however, that T. W. Richards (*J. Franklin Inst.*, July, 1924, p. 23) has shown that the heat of vaporization of mercury can be calculated by integrating the surface enclosed by internal pressure curves calculated from $m = 1.7$ and $n = 9.8$ with remarkable accuracy, the calculated and observed values being 55 kilojoules and 56 kilojoules, respectively. This calculation depends upon the extension of the range of applicability of the exponents to volumes (V_1) of five to ten times the original volume (V_0).

[10] Richards, THIS JOURNAL, **48**, 3067 (1926).

[11] I am indebted to Dr. R. H. Canfield of the staff of the Laboratory for the following transformation of exponents

$$p = \frac{\partial U}{\partial V} = \frac{\partial U}{3r^2\partial r} = -\pi\left(\frac{V_0}{r^3}\right)^m + (\pi_{\rho 0} + P_\theta)\left(\frac{V_0}{r^3}\right)^{n'}$$

$$\frac{\partial U}{\partial r} = -\frac{3\pi_0 V_0^m}{r^{3m-2}} + \frac{3(\pi_{\rho 0} + P_\theta)V_0^{n'}}{r^{3n'-2}}$$

$$U = -\frac{1}{1-m}\,\frac{\pi_0 V_0^m}{r^{3m-3}} + \frac{1}{1-n}\,\frac{(\pi_{\rho 0} + P_\theta)V_0^{n'}}{r^{3n'-3}}$$

$$= -\frac{A}{r^{\boldsymbol{m}}} + \frac{B}{r^{\boldsymbol{n}}}$$

$$\boldsymbol{m} = 3m - 3 \qquad m = \frac{\boldsymbol{m}}{3} + 1$$

Therefore

$$\boldsymbol{n} = 3n' - 3 \qquad n' = \frac{\boldsymbol{n}}{3} + 1$$

and also the critical disruptive volume, through Equation 7. The value obtained for the critical disruptive volume $V_{\text{critical}} = 1.52$, is, of course, identical with Joffe's value of $r_{\text{max.}} = 1.15$ ($r^3_{\text{max.}} = 1.52$), since the calculations of V_{critical} and $r_{\text{max.}}$ depend only upon the exponents which with the necessary transformation are identical in the two cases.

Introducing values for m, n', π and V_{critical} into Equation 6, $p_{\text{max.}}$ may be calculated and found to be 31,000 megabars. Converting this to kilograms per sq. mm. we obtain

$$p_{\text{max.}} = 316 \text{ kg./mm.}^2$$

which checks fairly closely with Joffe's value of 350 kg./mm.^{2}

This calculation, it is obvious, merely indicates that Richards' calculation of internal pressure gives a quantity which, after suitable transformation, is in definite agreement for sodium chloride with the constants in Born's equation. It must be taken as additional confirming evidence for the validity of Richards' equation.

It seems permissible, therefore, to carry out the calculation of disruptive negative pressures and critical disruptive volumes as outlined above for the metals, using the values for m, n' and π as given by Richards in one of his last papers.[12] From these values V_{critical} can be calculated by Equation 7, and with this $p_{\text{max.}}$ from Equation 6. The values thus obtained are listed in Table I.

These disruptive negative pressures may be taken as a measure of absolute cohesion. The conversion of this three-dimensional loading for metals to a one-dimensional loading seems impossible. Obviously it would be interesting to compare such a calculated tensile strength with the values for actual tensile strength. It is, however, by no means certain that a conversion of this sort would give a value strictly comparable to tensile strength values. It seems certain that the stress distribution in a breaking metal can by no means be represented as that occurring in two plane surfaces simply separated, but that there is a condition obtaining closely similar to the three-dimensional loading considered in the calculation above.[13]

Whatever might be the outcome of a calculation converting these disruptive negative pressures into true or absolute tensile strengths, it seems probable that the true or absolute tensile strengths would not be far from the calculated disruptive negative pressures, certainly of the same order of magnitude. Nothing further or more definite, however, can be said on this point.

Table I lists the tensile strengths of the pure metals corrected for reduction in area. It should be noted, however, that the reduction in area is always calculated from the area after fracture, which is usually less

---

[12] Richards, THIS JOURNAL, **48**, 3063 (1926).

[13] B. P. Haigh, *Proc. Int. Cong. App. Mech.*, Delft, **1924**, p. 328.

than the area which bears the maximum load. In other words, the values for the reduction in area are rather too large, making the corrected tensile strength somewhat too great. The literature is surprisingly deficient in trustworthy data on the tensile strength of pure metals and even more so in data on reduction in area, so that the figures given must be regarded as approximate except for the common metals such as copper, iron and aluminum.

TABLE I

DISRUPTIVE NEGATIVE PRESSURES AND CRITICAL DISRUPTIVE VOLUMES IN METALS, WITH OTHER RELATED DATA AT 30°

(m = 2.00 throughout)

	n'	π, Kilo-megabars	V_{critical}	$p_{\text{max.}}$ kg./mm.^{2}	$p_{\text{max.}}$ lbs./in.^{2}	Ultimate tensile strength[a] corrected, kg./mm.^{2}	Ultimate tensile strength[a] corrected lbs./in.^{2}
Lead	7.75	72	1.27	340	322,000	2.1	3,000**
Aluminum	5.85	191	1.32	734	694,000	120.0	170,000*
Silver	6.76	208	1.29	896	848,000	32.4	46,000**
Gold	9.10	243	1.24	1,262	1,195,000	(26.0)	(37,000)**
Copper	5.64	376	1.33	1,399	1,325,000	133.5	190,000**
Palladium	6.76	396	1.29	1,705	1,614,000	(38.0)	(54,000)*
Tantalum	6.49	455	1.30	1,900	1,801,000	(93.0)	(132,000)*
Platinum	7.81	465	1.26	2,210	2,090,000	(37.3)	(53,000)**
Nickel	5.65	508	1.33	1,890	1,792,000	126	180,000*
Cobalt	5.56	510	1.33	1,870	1,772,000	85.0	121,000*
Iron	4.84	587	1.305	1,884	1,781,000	120	170,000*
Tungsten	5.27	1020	1.35	3,570	3,379,000	1190	1,700,000**

[a] The numbers in parentheses in the last two columns are uncorrected for reduction in area, no data being available. Those with the single star are from "International Critical Tables," Vol. II; those with a double star are from the Bureau of Standards Circular No. 101, "Physical Properties of Material," 1924. The tensile strength values chosen were always the highest found for metals of high purity.

It may be seen immediately that the corrected tensile strength data are very much lower than the calculated disruptive negative pressures, even allowing for a factor of conversion. The explanation which Joffe[14] gives for the low tensile strength of sodium chloride crystals in air, namely, the presence of cracks inducing stress concentrations and a resultant low tensile strength, is directly applicable to the case of metals. In fact, the importance of very fine cracks in the behavior of metals is now becoming generally appreciated throughout metallurgical literature. It is not impossible that the surface of most metals should be cracked in an ultra-microscopic fashion, as indeed Kapitza[15] has demonstrated for bismuth. In addition, the phenomenon of slip which generally attends

---

[14] Ref. 2, pp. 56–66.

[15] Kapitza, *Proc. Roy. Soc. London*, **119**, 358 (1928); *cf.* Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253 (1929).

the failure of metals and alloys in the tensile test is conducive to the formation of a roughened surface (easily visible to the naked eye) through the sliding of crystalline blocks, producing reëntrant angles on the surface of the test piece with accompanying concentration of stress. Such a stress concentration should lead to the formation of cracks, with a resulting observed tensile strength much lower than that possible through the complete elimination of cracks. Any condition imposed upon the metal to make slip more difficult should, therefore, increase the tensile strength. In a completely isomorphous series of solid solutions the tensile strength is much greater than the calculated rule of mixtures value, as is the hardness. It does not seem likely that the forces of cohesion are much affected by the solid solution formation,[16] so that it is possible that the recognized increased resistance to slip originating in lattice distortion should restrain the tendency for the formation of cracks through slip. The improvement in tensile strength of alloy steels and of the "age-hardening" alloys by heat treatment may then be regarded as caused partly or perhaps wholly by improved resistance to slip.[17] The high absolute cohesion as indicated by $p_{\text{max.}}$ therefore, suggests that alloys have by no means reached their maximum possible values of tensile strength, and that a complete knowledge of the ultramicroscopic cracks and of the phenomenon of slip might lead to the development of extremely strong alloys.

Summary

1. It is pointed out that Richards' equation of state for solids can be used in the calculation of the negative pressures necessary for the disruption of metallic lattices and of the critical volumes at which the disruption should take place, a calculation not hitherto performed.

2. With exponents borrowed from Born after suitable transformation the method yields a disruptive negative pressure for sodium chloride in agreement with that which Joffe calculated from Born's potential energy equation.

3. Disruptive negative pressures and critical disruptive volumes are calculated for the twelve cubic metals for which Richards has given the constants in his equation of state.

4. The values of the disruptive negative pressures obtained suggest that the tensile strengths of metals and alloys have by no means reached their maximum possible values.

WASHINGTON, D. C.

---

[16] R. F. Mehl, THIS JOURNAL, 50, 73 (1928).

[17] Other factors besides simple solid solution formation may be operative in this respect, such as the production of fine hard particles in the slip planes, inter- and intracrystalline strains, unstable solid solutions, etc.