

The twins which were reported by Drew and Lewis [1] were also observed in the present work (Fig. 1). They resulted in the appearance of typical twin diffraction patterns which could sometimes be interpreted as belonging to (011) twins. The observable types of 2-dimensional defects (probably twins) in the structure and also the atoms' arrangement in the structure are still under investigation. The strong (300) reflection (2.8 Å) which was observed in all the reported investigations (see Fig. 2 in this work and footnote under Table I) may lead to the assumption that a stacking of 3 layers, each containing $3n$ formula units, is involved ($n = 1, 2, 3, \dots$). This implies that $3n$ formula units should fit into the new 754 \AA^3 unit cell. One adequate solution could be $\text{Si}_{10}\text{Al}_{15}\text{O}_{32}\text{N}_7$ recently found [5]. This composition can fit 3 times into the unit cell if a specific density of 2.9 is assumed. However, no definite conclusion concerning the possible compositions can be drawn at present.

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Solubility of hydrogen and bulk modulus in transition metals

Recently, the author [1] has shown that by correlating the heat of solution of hydrogen with spectroscopic data of neutral gaseous atoms, the solution process of hydrogen in the transition metals involves transfer of an s electron from the metal to hydrogen, or vice versa with changes in the electronic configuration of the metals.

There is, however, still controversy as to whether or not hydrogen dissolved in a metal has any effective size or whether chemical bonding effects are important. McQuillan [2] has suggested that interstitial atoms are too small to have any meaningful size. Ebisuzaki and O'Keefe [3] has expressed a similar view. In contrast, however, several authors [4–7] have considered the size factor to be important. Oriani [8] has shown, from the calculation of partial molar volume of hydrogen in various metals, that the disturbance

produced by the hydrogen can be very large, and that it varies from one lattice to another. The importance of considering volume changes in connection with the thermodynamic behaviour of solid solutions as a function of solute atom concentration has been pointed out by Wagner [9]. Armoult and McLellan [10] have measured the variation of Young's modulus of austenite produced by increasing the carbon content. The decrease in the Young's modulus was contrasted with the recent work of Wriedt and Oriani [11] on the effect of dissolved hydrogen on the Young's modulus of Ta, Nb, and V, in which the presence of interstitial species was found to increase linearly.

The purpose of this letter is to show that the heats of solution of hydrogen in metals can be correlated to the bulk modulus, which is a direct measure of the strength of bonding in metals. Considering the solubility of hydrogen in a metal, we write the equation of solution in the form

$$\frac{1}{2}H_2 = H_M \quad (1)$$

where a subscript M refers to hydrogen dissolved in the metal. From standard thermodynamic considerations, we can easily deduce Sievert's law for the concentration of dissolved hydrogen

$$H_M = \exp(-\Delta G^0/RT)P_{H_2}^{1/2} \quad (2)$$

where $\Delta G^0 = \Delta H^0 - T\Delta S^0$ is the standard free energy change for Reaction 1. To a good approximation, the solubility can be expressed as

$$\log H_M = \frac{-\Delta H^0 + T\Delta S^0}{2.303 RT} \quad (3)$$

at a hydrogen pressure of one atmosphere. The entropy term in Equation 3 describes the change in order when hydrogen atoms are transferred from the diatomic gas to interstitial sites in the metals. One would expect the entropy to be approximately independent of the nature of solvent metals for a given gas. The heat of solution of hydrogen, ΔH^0 , is, therefore, a measure of the ability of solvent metals to dissolve hydrogen without forming hydrides.

The heats of solution for hydrogen in the transition metals, ΔH^0 , which are taken from [1] are shown in Figs. 1a to 3a as a function of the atomic radius for each series. In all three series, the heat of solution for hydrogen increases with the atomic radius as far as Group VIA, after which a difference exists between the first and latter series. In the second and third series, the ΔH^0 continues to increase and reaches maximum values. In the first series, ΔH^0 of α -Mn is anomalous, as would be expected from its abnormal crystal structure, but otherwise, there is little change on passing from Fe \rightarrow Co \rightarrow Ni.

The heat of solution of hydrogen at zero solubility is shown as a broken line, which separates (a) those metals dissolving hydrogen exothermally and forming generally stable hydrides, and (b) those metals dissolving endothermally.

An interesting sidelight is provided from the bulk modulus of metals. This property is a direct measure of the bonding strength, that is, of the resistance of the atoms to being pressed together and, therefore, to being pulled apart. Consequently, strong bonding is indicated by a high, bulk modulus and a low compressibility. In Figs. 1b to 3b, the bulk modulus at room temperature, B [12], divided by the atomic volume, V [13], is

shown as a function of the atomic radius for each series. It is readily apparent that the periodic variations of the B/V in Figs. 1b to 3b follow a pattern very similar to those of ΔH^0 in Figs. 1a to 3a.

On the ascending branch, the progressive addition of electrons caused by an increase in atomic number along a series acts in parallel to the electron gained through addition of hydrogen atoms: both increase the bond strength, though the latter introduces directionality in bonding, with embrittlement. On the descending branch, both types of electron addition are bond-weakening.

Since hydrogen is considered as a metal, it is instructive to estimate the bulk modulus of metallic hydrogen. It is known that the bulk modulus is related to the cohesive energy in alkali and alkali earth metals [14]. In order to find a relationship between the bulk modulus and cohesive energy, the cohesive energy of non-transition metals [15] (except Cn, Au, and Ag), E_c , divided by the atomic volume, V , is plotted against B/V in Fig. 4 and yields a linear relationship represented by

$$(E_c/V) = 9.38 (B/V) + 1.0 \quad (4)$$

The E_c/V of metallic hydrogen can be calculated if the cohesive energy is replaced by the energy required to ionize hydrogen atoms. Since the ionization potential is 13.51 eV or 312 kcal mol⁻¹ and the atomic volume 14.1 cm³ mol⁻¹, it yields 22.13 kcal cm⁻³ for hydrogen from the above Equation 4, which is equal to $B/V = 2.25 \times 10^{-7}$ kg cm⁻⁵. The B/V of metallic hydrogen is quite high, indicating that the hydrogen atom is tightly bound in the metallic state.

The B/V of metallic hydrogen is shown as a broken line in Figs. 1b to 3b, which again makes a division line between the exothermic and endothermic metals. This line is, of course, equal to the heat of solution of hydrogen at zero solubility in Figs. 1a to 3a. Close examination of Figs. 1 to 3 shows that the bulk moduli of all the exothermic metals are lower than that of metallic hydrogen. The dissolution of hydrogen atoms in the metals causes a decrease in the strength of bonding, which in turn causes a decrease in the cohesive energy and an increase in the lattice spacing. Since the metal-metal separ-

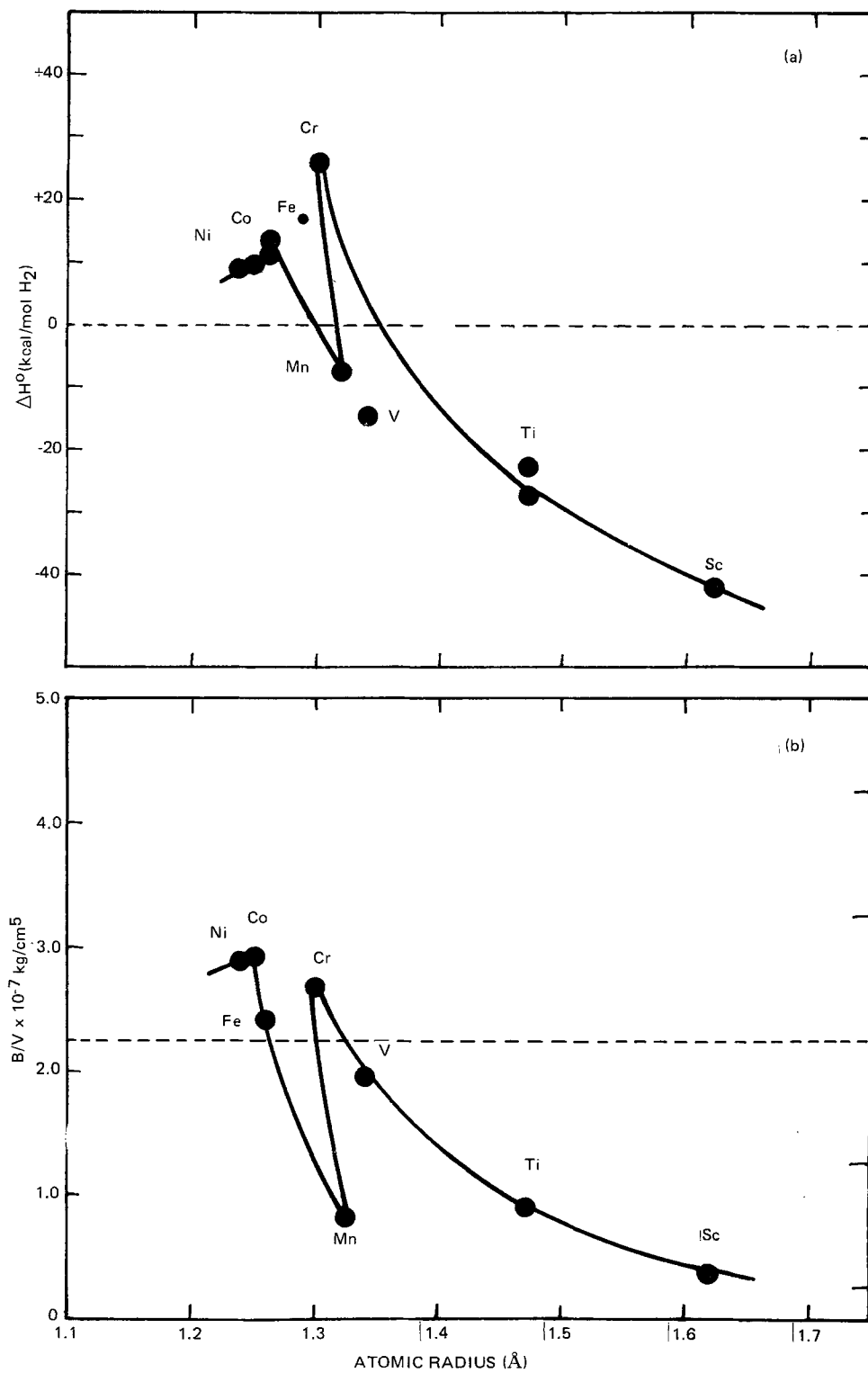


Figure 1 (a) The variation of ΔH° , and (b) the variation of B/V as a function of the atomic radius in the first transition metal series.

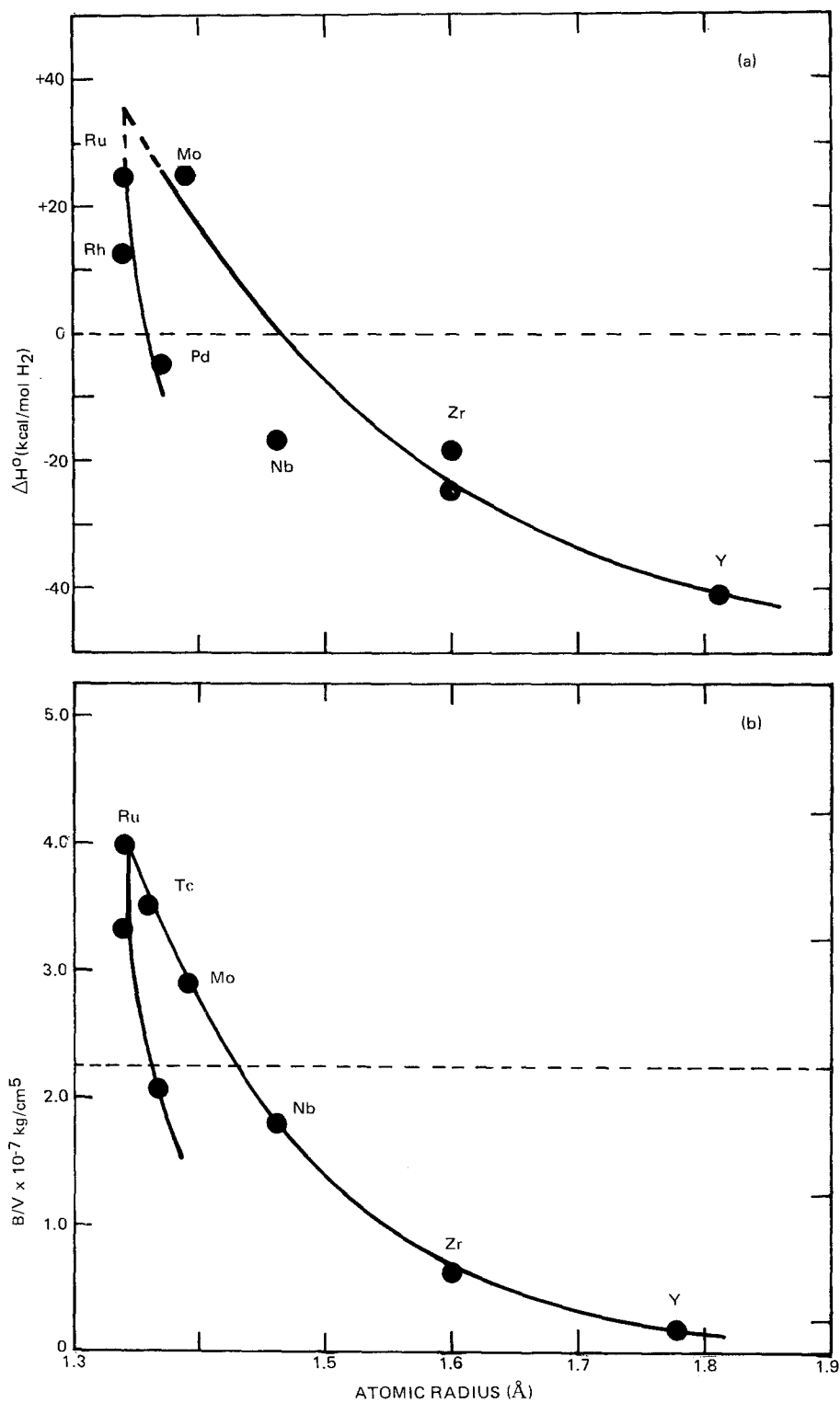


Figure 2 (a) The variation of ΔH^0 , and (b) the variation of B/V as a function of the atomic radius in the second transition metal series.

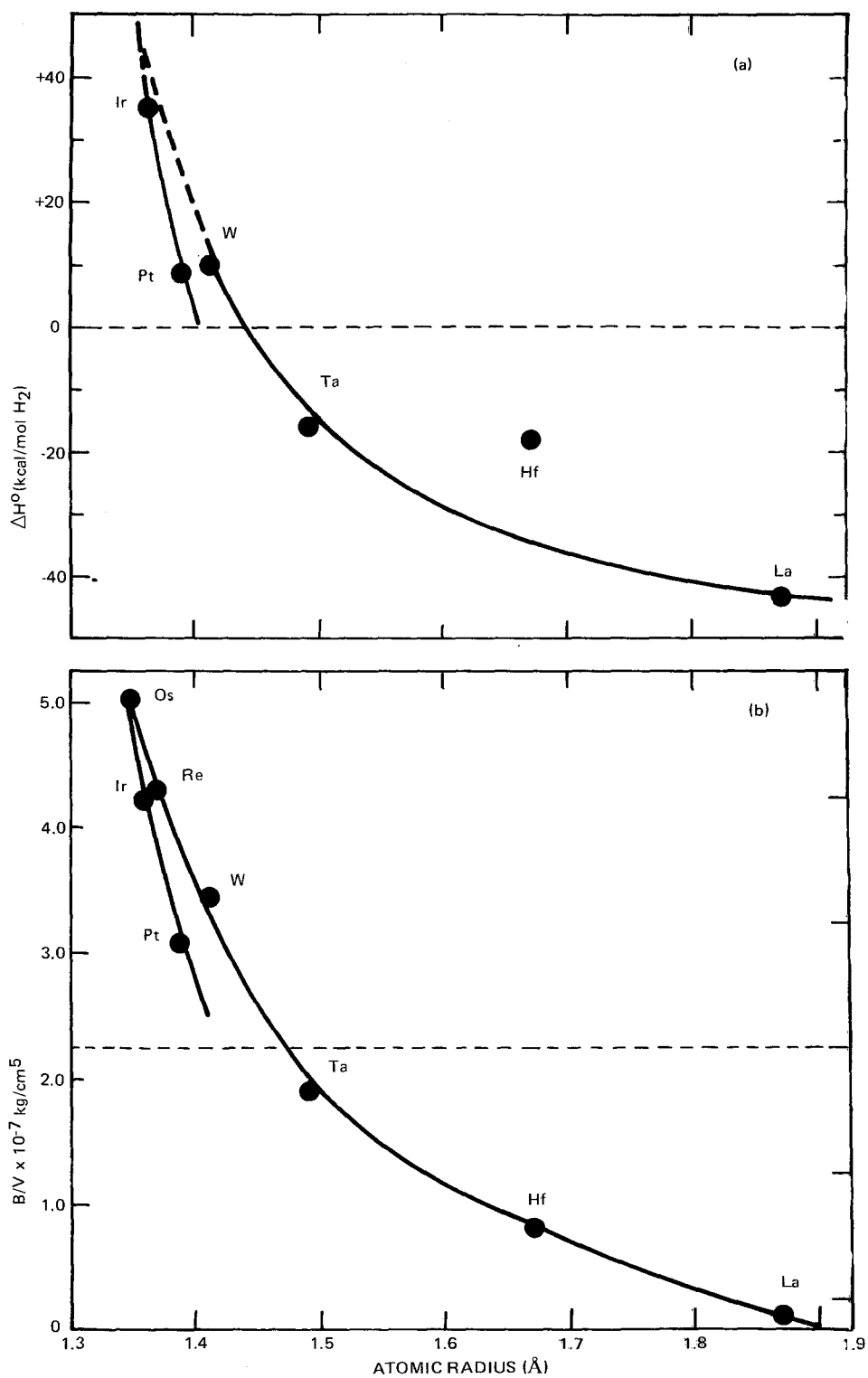


Figure 3 (a) The variation of ΔH° , and (b) the variation of B/V as a function of the atomic radius in the third transition metal series.

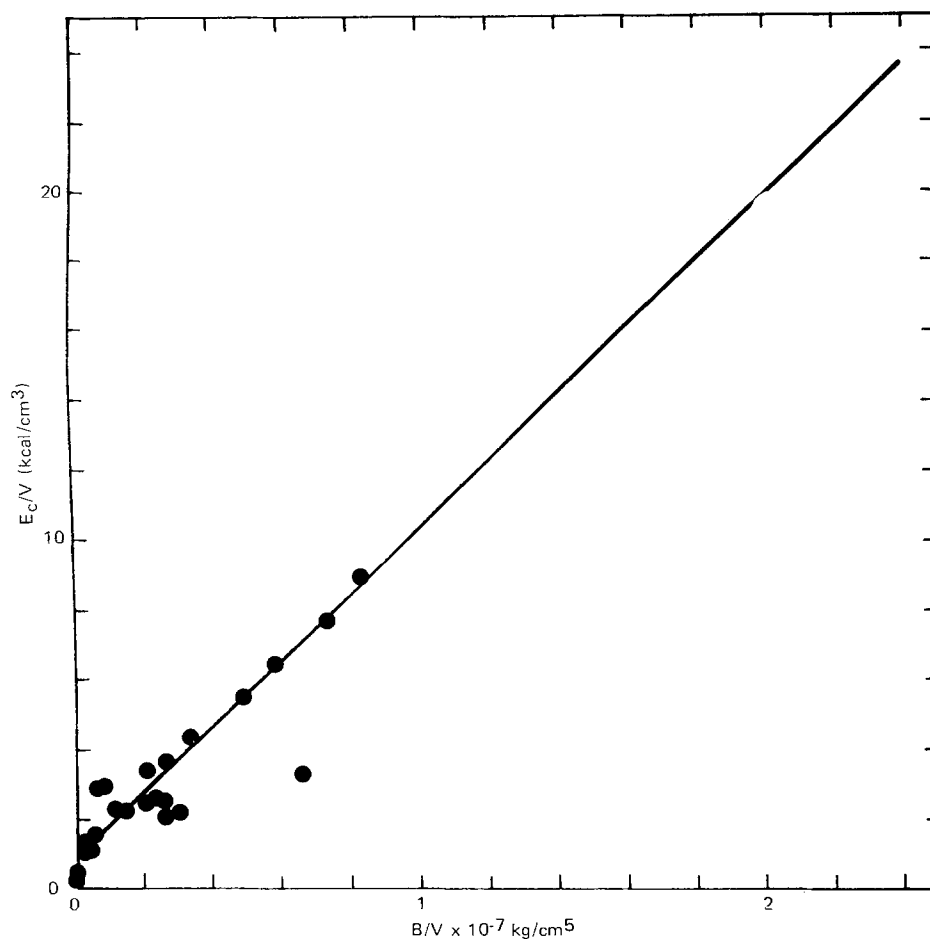


Figure 4 A plot of E_c/V and B/V in non-transition metals.

ation becomes much larger than the pure metals, the electron cloud of a metal in the metal–hydrogen bond will tend to be pulled toward the hydrogen, which then acquires the character of a negative ion, yet is not H^- , as is usually assumed, but an ion formed by greater or less displacement of the relative maximum of electron density in the direction of the core of an hydrogen atom. Thus, the bond becomes more ionic as the difference between the bulk moduli of hydrogen and metal grows greater.

On passing the broken line, on the other hand, the metals become endothermic and the bulk moduli of the metals become greater than that of metallic hydrogen. When hydrogen is dissolved in the metal, which is much less compressible, the much stronger bonding forces of the metal control the structure to such an extent that the solubility is much smaller than would be expected and it

gives way to hydrogen in solution rather than the formation of hydrides.

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