and E. Pytte. Samples of $2H$-TaSe$_2$ were provided by S. F. Meyer. It is a pleasure to thank these people.

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[10] The value of 85 cm^{-1} is based on the neutron scattering data of Moncton, Axe, and Di Salvo (Ref. 3). The LA phonon dispersion of $2H$-NbSe$_2$ at 300 K shows only a very weak dip near the CDW wave vector and only a very weak temperature dependence. This is consistent with the assumption that any Kohn anomaly is quite weak at 300 K. Furthermore, we note that our choice of $\omega_0 = 85\ \mathrm{cm}^{-1}$ really represents the smallest likely value; any large value would result in even lower estimate for the value of Λ, consistent with the fact that only a small fraction of the Fermi surface is affected by the CDW transition.

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Pronounced Isotope Effect in the Superconductivity of HfV$_2$ Containing Hydrogen (Deuterium)*

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Superconducting transition temperatures of HfV$_2$H$_x$ and HfV$_2$D$_x$ have been measured in the composition ranges $x = 0-1.5$ and $x = 0-1.0$, respectively. Hydrogen or deuterium absorption is found to decrease T_c of HfV$_2$. Pronounced isotope effects have been observed. At $x = 1$, hydrogen absorption reduces T_c by 4.8 K while deuterium absorption reduces T_c by 6.9 K with respect to HfV$_2$.

Superconductivity in metal-hydrogen systems has recently been a subject of considerable interest due to the possibility of finding high T_c in these materials via an attractive pairing interaction arising from the high-frequency vibrational modes of the proton lattice. Detailed studies have so far been carried out on the hydrides and deuterides of thorium[1] and palladium.[2-5]

It is interesting to note that although Pd itself is not superconducting, Pd-H and Pd-D exhibit T_c values as high as 9 and 11 K, respectively.[3-5] Moreover, in Pd-Cu-H, Pd-Ag-H, and Pd-Au-H systems, high T_c values of 16.6, 15.6, and 13.6 K, respectively, could be attained.[6] Since, in the absence of hydrogen, these alloys are nonsuperconducting, it is evident that the appearance of superconductivity in the hydrides of Pd and Pd–noble-metal alloys is not just a result of the quenching of spin fluctuations as was supposed earlier.[7] It seems to have its origin[8,9] in the enhanced pairing interaction arising from the high-frequency optic phonon modes[10] associated with the proton (or deuteron) lattice.

Another interesting feature is the discovery that Th$_4$H(D)$_{15}$ exhibits no detectable isotope effect[1] while Pd-H(D) exhibits a pronounced reverse isotope effect[3-5] (T_c for PdH ~ 9 K and for PdD ~ 11 K). The reverse isotope effect in PdH(D) has been explained separately on two different models. The first model[8] involves the influence of the optic modes on the electron-phonon coupling in PdH and PdD. The second model[4] attributes the effect to the difference in electronic structure due to the H atom spending more time in the proximity of the Pd atom than the D atom.

In view of these interesting features, further studies are needed to understand the nature of superconductivity in metal-hydrogen systems. The hydrides of the cubic Laves ($C15$) phase alloys Hf$_x$Zr$_{1-x}$V$_2$ are well suited for a detailed investigation because of their high T_c and H_{c2} values[11-15] [$T_c = 8.6$ to 10.1 K, $H_{c2}(4.2) = 100$ to 230 kOe] and ability to absorb large quantities of hydrogen at room temperature and moderate pressures.[16,17] At 300 K and 500 psi pressure, the amount of H (or D) that is introduced ranges[17] from 1.5 to 1.85 H (or D) atoms per metal atom in the compositions $Hf_xZr_{1-x}V_2$. The crystal structure does not change, but the cubic lattice parameter is increased considerably upon introducing hydrogen.[16,17]

In this Letter we report the results of T_c measurements on $HfV_2H(D)_x$ alloys. Of special interest are two remarkable observations. (i) T_c decreases rapidly upon introducing H or D into HfV_2. (ii) A large "normal" isotope effect is observed in contrast to the behavior of $PdH(D)_x$ and $Th_4H(D)_{15}$ mentioned earlier.

The HfV_2 alloy samples were prepared by induction melting of the elements, followed by annealing at 800°C for 100 h. The samples were then alloyed with high-purity hydrogen or deuterium at room temperature and 500 psi pressure to yield the composition $HfV_2H(D)_{4.54}$. A range of $HfV_2H(D)_x$ compositions was made by equilibrating various ratios of $HfV_2H(D)_{4.54}$ with virgin HfV_2 in sealed quartz tubes at 450°C for 48–72 h. X-ray diffraction revealed the $C15$ structure for all compositions. The variations of the lattice parameter in the composition range $x=0$ to 1.25 is shown in Fig. 1.

Most of the samples were powdered, because of absorption of hydrogen. A sensitive inductance bridge circuit was used[18] to measure T_c. H_{c2} was also measured as a function of temperature in some samples using a 120-kOe superconducting magnet. The superconducting-normal transitions were rather wide (~0.8 K). T_c was measured as the temperature at which dV/dT was a maximum, V being the voltage signal proportional to the imbalance in the bridge circuit caused by the transition. T_c values obtained in this manner were reproducible to within 0.1 K.

T_c data for various $HfV_2H(D)_x$ compositions are presented in Fig. 2. The effect of both hydrogen and deuterium absorption is to reduce T_c. At $x=1$, hydrogen absorption reduces T_c by 4.8 K while deuterium absorption reduces T_c by 6.9 K. The reduction in T_c seems also to be accompanied by a reduction of H_{c2}, as exemplified by the curves of H_{c2} vs T for HfV_2, $HfV_2H_{0.5}$, and $HfV_2D_{0.5}$ (Fig. 3).

It is interesting to note that, if one denotes by $\Delta T_c(x)$ the reduction in T_c from the parent HfV_2 upon the addition of x moles of H or D, one observes that

$$\Delta T_c(x) \propto M^{0.5}, \tag{1}$$

where M is the mass of H or D, as the case may be. A clear interpretation of this result may have to await experimental information on the electronic structure and phonon spectra of $HfV_2H(D)_x$. Nevertheless, since the lattice parameters of HfV_2H_x and HfV_2D_x are very nearly the same (Fig. 1), one may surmise that the acoustic phonon characteristics associated with the metal atom vibrations should be nearly the same for the two cases and therefore may not be responsible for the pronounced T_c difference between HfV_2H_x and HfV_2D_x. Hence, it indicates that the difference may arise from the high-frequency local modes associated with the H or D atoms. There is also the possibility that the isotope effect is a consequence of the difference be-

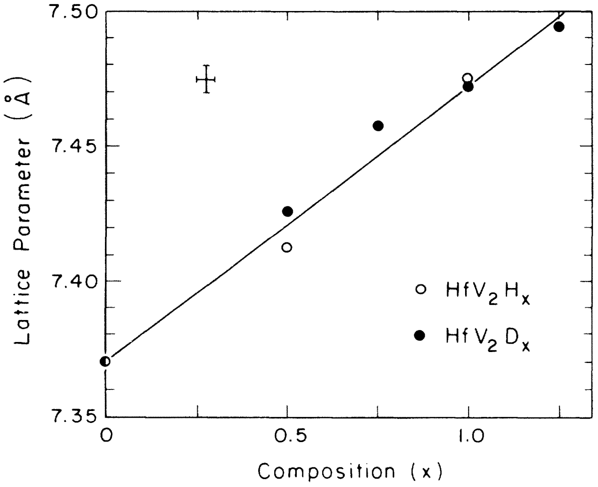

FIG. 1. Cubic lattice parameter versus x in HfV_2H_x and HfV_2D_x.

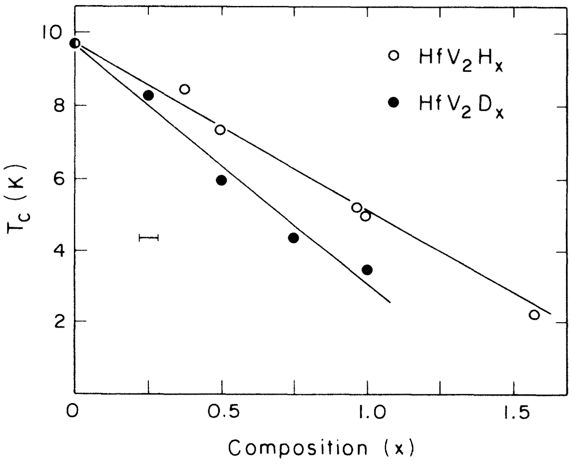

FIG. 2. Variation of T_c with x in HfV_2H_x and HfV_2D_x.

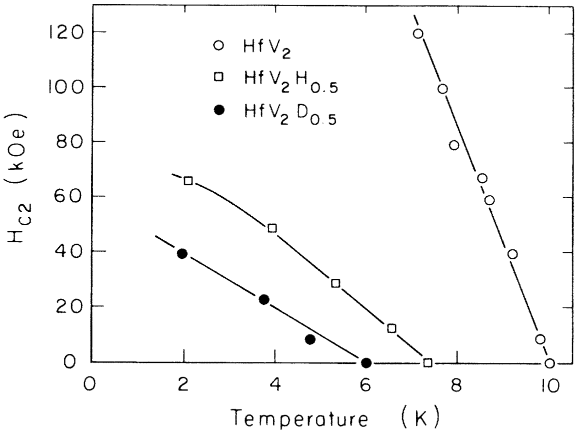

FIG. 3. H_{c2} of HfV_2, $HfV_2H_{0.5}$, and $HfV_2D_{0.5}$ as a function of temperature.

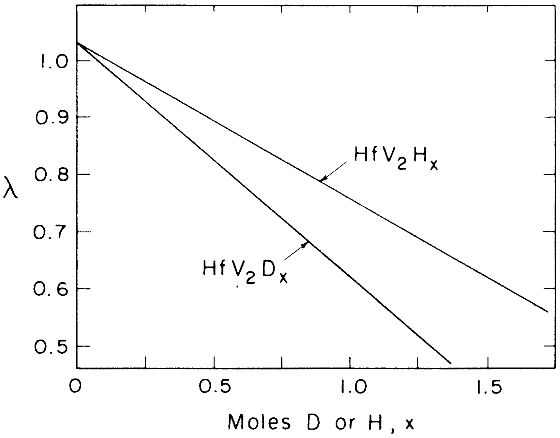

FIG. 4. The electron-phonon coupling constant λ, as a function of composition in HfV_2H_x and HfV_2D_x.

tween the electronic structure of HfV_2H_x and HfV_2D_x, as will be discussed later.

For a discussion of the results one may use McMillan's expression[19] for strong-coupled superconductors which may be written

$$T_c=\frac{\theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \tag{2}$$

where θ_D is the Debye temperature, μ^* is an electron-electron interaction parameter, and λ is the mass enhancement factor arising from electron-phonon interaction. It is of interest to obtain λ as a function of H or D concentration in HfV_2H_x and HfV_2D_x. One may reasonably choose $\mu^*\sim0.13$ for transition metals.[19,20] Specific-heat measurements of HfV_2 by Rapp and Vieland[21] yield $\theta_D = 190$ K. Similar measurements have not yet been made for alloys of HfV_2 with H and D. For the present, if one assumes the same value of θ_D for the superconducting compositions HfV_2H_x and HfV_2D_x, one obtains the variation of λ with x as shown in Fig. 4. These plots would be changed if future heat-capacity measurements show that the above assumption is not valid. It may be mentioned, in passing, that in the Pd-H system very little change in θ_D was observed upon hydrogenation, from low-temperature heat capacity measurements.[22]

The parameter λ obtained by the above procedure is very helpful in the understanding of the mechanism of superconductivity in various systems. For pure metals, one may follow McMillan[19] in writing

$$\lambda=n(E_F)\langle I^2\rangle/M\langle\omega^2\rangle, \tag{3}$$

where $n(E_F)$ is the density of states at the Fermi level, $\langle I^2\rangle$ is an average over the Fermi surface of the square of the electron-phonon matrix element, M is the atomic mass, and $\langle\omega^2\rangle$ is the second moment of the phonon frequencies as defined by McMillan.[19] For alloys containing H, D, or other light atoms, it has been suggested[23,9] that λ can be separated into contributions arising from the light and heavy atoms. However, a detailed interpretation of the measured λ values for HfV_2H_x and HfV_2D_x must await heat-capacity and other measurements on these systems. These are being planned for the near future.

Potentially, the data on $(dH_c/dT)_{T_c}$ are capable of providing information on the electronic structure through the relation[24]

$$-(dH_{c2}/dT)_{T=T_c}=0.439\times10^3\rho_0\gamma, \tag{4}$$

where ρ_0 is the residual resistivity in units of 10^{-6} Ω·cm and γ is in units of mJ cm^{-3} K^{-2}. For HfV_2, our measurements yield $\rho_0 = 62$ μΩ·cm in agreement with Inoue, Tachikawa, and Iwasa[14] and the specific heat measurements[21] give $\gamma = 1.881$ mJ cm^{-3}. Using the experimental values of ρ_0 and γ one obtains for HfV_2,

$$-(dH_{c2}/dT)_{T=T_c,\,\text{cal}}=61.2\text{ kOe K}^{-1},$$

in reasonable agreement with the experimentally determined value (Fig. 3)

$$-(dH_{c2}/dT)_{T=T_c,\,\text{exp}}=43\text{ kOe K}^{-1}.$$

If ρ_0 values for HfV_2H_x and HfV_2D_x were available, the above procedure could be used to obtain γ and hence $n(E_F)$ as a function of x. Since the samples crumble into powder, it is difficult to perform these measurements. If, however, one assumes for example, that ρ_0 is nearly the same for

$HfV_2H_{0.5}$ and $HfV_2D_{0.5}$, the data on $(dH_{c2}/dT)_{T=T_c}$ (Fig. 3) indicate that γ for $HfV_2H_{0.5}$ is nearly 1.4 times the γ of $HfV_2D_{0.5}$. Hence, at least qualitatively, it is capable of explaining the difference in λ between $HfV_2H_{0.5}$ and $HfV_2D_{0.5}$ (Fig. 4). Thus, at this stage it is not possible to say whether the strong isotope effect arises from the high-frequency local modes or the differences in $n(E_F)$.

In conclusion, it is clear that the influence of hydrogen on the superconductivity of different metal and alloy systems is quite varied. In some systems T_c is enhanced (e.g., Pd-H and Th_4H_{15}) while in others it is depressed (e.g., HfV_2-H). The isotope effect on T_c with respect to H and D shows pronounced "normal" (e.g., HfV_2-H or D), "reverse" (e.g., Pd-H or D) or very weak (e.g., Th_4H_{15}) trends. Much further work is needed to obtain a clear understanding of the superconducting behavior of metal-hydrogen systems.

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Band-Structure Effects in the Selective Adsorption of Helium on Sodium Fluoride*

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Splitting of energy levels of atoms bound to a crystal surface have been observed in atomic beam scattering.

A free atom approaching a crystal surface may undergo a "selective adsorption" transition into a state in which it is bound to the surface but translating rapidly across it. The phenomenon was first observed by Frisch and Stern,[1] and the basic explanation was put forth by Lennard-Jones and Devonshire[2] as a resonance between the initial free-particle energy $\hbar^2k^2/2m$ (where $\vec{k}$ is the wave vector and m the mass of the atom) and the final-state energy

$$E_{\text{final}} = E(j, \vec{K}'). \tag{1}$$

Here, j is the "vibrational quantum number" associated with the motion normal to the surface and $\vec{K}'$ is the wave vector of the Bloch wave describing the parallel motion. Because of the conservation of crystal momentum in the two-dimensional periodic potential near the surface, $\vec{K}'$