Lattice Dynamics of Dilute Impurities in Transition Metals: An Empirical Correlation*

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Certain lattice-dynamical properties of dilute Fe impurities in cubic transition-metal hosts are found from Mössbauer-effect studies to be correlated in a simple and unexpected way with the host properties and the impurity mass. The correlation is consistent with the hypothesis that the effective force constant associated with impurities is proportional to the geometric mean of the force constants for the impurity in bulk and for the host lattice in bulk. This result has applicability to testing of the McMillan theory of superconductivity.

In this Letter, we report systematics of Mössbauer-effect studies of the lattice-dynamical properties of iron atoms as dilute impurities in a series of cubic transition-metal hosts. We find that a particular ratio of averages over the impurity phonon density-of-states distribution important in strong-coupling superconductor theory is correlated in a simple and unexpected manner with the Debye temperature of the host lattice and with the ratio of the impurity mass to the host mass. The correlation obtained is functionally different from that which would be expected on the basis of several impurity theories. The existence of this correlation has implications for understanding of the systematics of superconducting transition temperatures using the theories of McMillan and of Hopfield.

The lattice dynamics of transition metals are yet to be calculated from first principles. The primary difficulties stem from the complexity of the d-electron shells. Recently, it has been shown that the binding energy of transition metals cannot be calculated in the same simple way as in the alkali metals: The s-d hybridization and the partial occupancy of the broad transition-metal d band play a greater role than was suspected.[1] The problem of the lattice dynamics of a transition-metal impurity in a transition-metal host is even more difficult. The lattice dynamical parameters are presumably correlated in some complicated manner with the electronic structure of the host, the particular impurity, the impurity mass M_i, and the host mass M_h. (The subscripts i and h denote the impurity and the host properties, respectively.) Despite the apparent hopelessness of the problem, the importance of the lattice dynamical problem and in particular its relevance to the theory of strong-coupling superconductors[2,3] makes it important to search for correlations with other properties of the transition metals.

The primary results of our study are shown in Fig. 1. The ordinate is the ratio of two expectations over the phonon density of states at Fe impurity sites for various host lattices. The abcissa is the Debye temperature of the host lattice divided by the square root of $R \equiv M_i/M_h$ (the ratio of the impurity-atom to the host-atom mass). The solid circles are obtained from high-temperature measurements and the open circles are based upon low-temperature measurements. The curves are least-square fits through the data. Also shown is a theoretical curve which represents the prediction of a simple theory for the impurity. We now explore the quantities plotted in the figure and relate them to experiment and to theory.

Because of the complexity of the lattice-dynamical problem of an impurity, it is desirable to utilize systems which are potentially susceptible to theoretical interpretation. We consider alloys with sufficiently small impurity concentrations that the interaction of impurities with one another can be neglected. Such systems have been analyzed by Elliot and Dawber[4] in the harmonic mass impurity model and by Visscher for the case with impurity force constants of the impurity differing from host force constants.[5]

It is usually sufficient to know the phonon density of states, $g(\omega)$, in order to calculate the important properties associated with the lattice dynamics of a material. In particular, the lattice

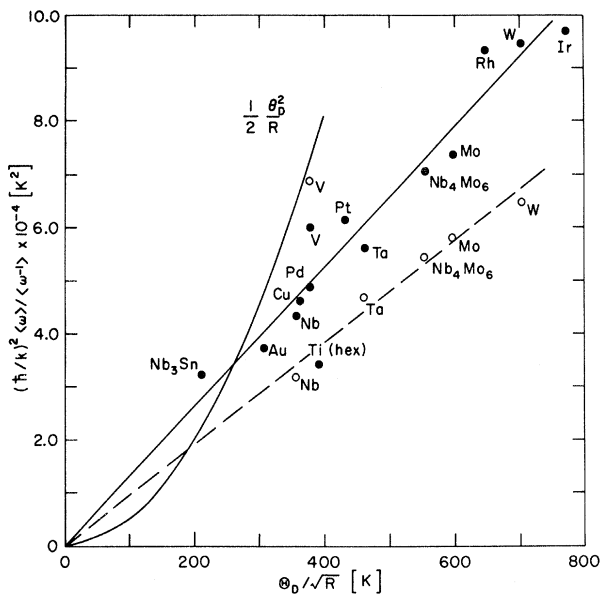

FIG. 1. The linear correlation of the high-temperature (closed circles) and low-temperature (open circles) McMillan phonon parameter, measured at an Fe^{57} impurity in the cubic transition metal series, with the Debye temperature of the host and the square root of the impurity-to-host-mass ratio. The best line through the origin for the high-temperature data has a slope of 133 ± 3. The low-temperature slope is 95 ± 2. Here the high-temperature parameter has been multiplied by $\frac{3}{2}$, the factor which corrects the value to the low-temperature value calculated from the Debye model, and is approximately correct for the mass defect theory of Dawber and Elliott (Refs. 4 and 7). The Debye model theoretical expectation, $\theta_D^2/2R$ [see Eq. (8)] is also displayed.

properties can be expanded in terms of the moments of $g(\omega)$, i.e.,

$$[\omega^l] \equiv \int_0^\infty \omega^l g(\omega) d\omega, \quad [\omega^0] \equiv [1] \equiv 1. \tag{1}$$

The density of phonon states for the impurity $g_i(\omega)$ may be modified substantially from the host phonon density $g_h(\omega)$ if either (a) the impurity atom has a different mass than the atomic mass of the host ($R \neq 1$) or (b) the force constants of the impurity are different than those of the host. [For example, for R less than some critical R dependent on the impurity and host force constants and $g_h(\omega)$, a mode localized on the impurity will exist at a frequency greater than the maximum frequency of the host phonons. For larger R there will be a broad virtual local mode imbedded in the allowable host phonon frequencies.[4]]

The Mössbauer effect measures the second-order Doppler shift $(\Delta E/E)_{2D}$ and the recoil-free fraction $f(T)$ and, except for unusual circumstances in which localized modes play a dominant role, these quantities are related to the thermal averages

$$-2c^2(\Delta E/E)_{2D} = \langle \dot{u}^2 \rangle_i = (3\hbar/M_i)\langle \omega^{+1} \rangle_i, \tag{2a}$$

$$-3\lambda\!\!\!^{-2} \ln f(T) = \langle u^2 \rangle_i = (3\hbar/M_i)\langle \omega^{-1} \rangle_i. \tag{2b}$$

Here u is the displacement of the atom, and the thermal averages are denoted by

$$\langle \omega^l \rangle \equiv \int_0^\infty (\bar{n} + \tfrac{1}{2}) \omega^l g(\omega) d\omega. \tag{3}$$

The reduced wavelength of the gamma radiation of energy E is $\lambda\!\!\!^{-} \equiv \hbar c/E$, and $\bar{n}$ is the occupation number of the states of energy $\hbar\omega$. At high temperatures (denoted by a subscript ∞) $\bar{n}_\infty \to kT/\hbar\omega$ and therefore

$$\langle \omega^l \rangle \to (kT/\hbar)[\omega^{l-1}]. \tag{4a}$$

At low temperatures $n \to 0$ and

$$\langle \omega^l \rangle = \tfrac{1}{2}[\omega^l]. \tag{4b}$$

The Mössbauer effect can be used to determine $[\omega^0]$, $[\omega^1]$, $[\omega^{-2}]$, and $[\omega^{-1}]$ from the high- and low-temperature energy shifts and from the high- and low-temperature recoil-free fractions, respectively. The parameter $\rho \equiv \langle \omega \rangle / \langle \omega^{-1} \rangle$ is important in the theory of strong-coupling superconductors; we emphasize systematic correlations of this parameter with other physical properties of the host metal and the impurity. Experimental details will be published elsewhere.[8]

In previous work[7] we have shown that the McMillan phonon parameter at an impurity site, $\rho_i \equiv \langle \omega \rangle_i / \langle \omega^{-1} \rangle_i$, can be determined from a parameteric plot of $\ln f(T)$ vs $\Delta E(T)$ where the parameter is T. This plot is found to be nearly a straight line. The high-temperature value of ρ_i is inversely proportional to the slope of the line.

The low-temperature value of the phonon parameter, $\rho_{i,0}$, has been determined by utilizing our new high-precision shift and absolute $f(T)$ measurements. The $\langle \omega^{-1} \rangle_{i,0}$ is determined by using Eq. (2b) directly. We have found that the temperature dependence of the shift agrees excellently with that calculated for the Debye model (the characteristic temperatures are, of course, different from those obtained in other ways). We have used this dependence as a spline to determine the $T = 0$ second-order Doppler shift and through Eq. (2a) we have determined $\langle \omega^{+1} \rangle_{i,0}$.

The observed high-temperature phonon parameters $\rho_{i,\infty}$ for the impurity in the Mössbauer investigation are closely related to the equivalent high-temperature phonon parameters of the host atoms, and are relatively independent of the de-

tails of any theory of the lattice. In the high-temperature limit, the momentum coordinates of the host as well as the impurity atoms are independent in the usual Hamiltonian. Hence, classical equipartition of kinetic energy assures that

$$\tfrac{3}{2}kT = \tfrac{1}{2}M_h\langle\dot{u}^2\rangle_{h,\infty} = \tfrac{3}{2}\hbar\langle\omega\rangle_{h,\infty}, \quad (5a)$$

$$\tfrac{3}{2}kT = \tfrac{1}{2}M_i\langle\dot{u}^2\rangle_{i,\infty} = \tfrac{3}{2}\hbar\langle\omega\rangle_{i,\infty}, \quad (5b)$$

independent of differences in the force constants of the impurity and the host atoms. Because the new Mössbauer data for all samples (excepting Cu and Au) show little evidence of anharmonic effects,[8] we assume the adequacy of the harmonic approximation.

In the harmonic approximation, and the high-temperature limit, the analog to the virial theorem yields

$$\tfrac{1}{2}M_h\langle\dot{u}^2\rangle_{h,\infty} = K_h\langle u^2\rangle_{h,\infty} = \frac{3K_h\hbar}{M_h}\langle\omega^{-1}\rangle_{h,\infty}, \quad (6a)$$

$$\tfrac{1}{2}M_i\langle\dot{u}^2\rangle_{i,\infty} = K_i\langle u^2\rangle_{i,\infty} = \frac{3K_i\hbar}{M_i}\langle\omega^{-1}\rangle_{i,\infty}, \quad (6b)$$

where K_h and K_i may be considered as effective force constants of the host atoms and the impurity atoms, respectively. Combining (5) and (6), we have

$$\rho_{i,\infty} = \frac{\langle\omega\rangle_{i,\infty}}{\langle\omega^{-1}\rangle_{i,\infty}} = \frac{K_h}{RK_i}\rho_{h,\infty}. \quad (7)$$

Thus, the McMillan parameter measured at the impurity atom depends upon host properties only through the force constants and the mass ratio.

An assumption often made for the class of bcc transition metals is that the phonon density of states scales with the Debye temperature θ_D:

$$[\omega^n] = \int_0^\infty g(\omega)\omega^n d_\omega = Cn(\{k\theta_D\}/\hbar)^n,$$

where the C_n are independent of the host material.

Putting this result in Eq. (7), we obtain

$$\rho_{i,\infty} = \rho_{h,\infty}\frac{K_i}{RK_h} = \frac{C_0}{C_{-2}}\frac{K_i}{K_hR}\left\{\frac{k\theta_D}{\hbar}\right\}^2 \quad (8)$$

in agreement with the exact theory by Elliott and Dawber for $K_i = K_h$.[4] {For the Debye model $C_l = [3/(3+l)]$, $l \neq -3$, leading to $C_0/C_{-2} = \frac{1}{3}$ and $\rho_\infty \cong \frac{2}{3}\rho$.}

Using experimental values for $\rho_{i,\infty}$, assuming the harmonic approximation, and making the scaling hypothesis described above, it is possible to measure K_i/K_h provided we can estimate C_0/C_{-2}.

The data in Fig. 1 may now be discussed using this notation. The ordinate is the quantity $\rho_{i,0}$ in units of temperature. The closed circles are $\frac{3}{2}\rho_{i,\infty}$. The factor of $\frac{3}{2}$ approximately scales the high-temperature values to low-temperature values for most $g(\omega)$.[7] The abcissa is $\theta_D/\sqrt{R}$. The solid line is the best straight-line fit to the high-temperature data through the origin. The slope is 133 ± 3. The Ti point has been added to show how a hexagonal host would differ from the cubic ones and the Nb_3Sn point is from Mössbauer data for Sn^{119} in this β-W structured host. The dashed curve is obtained from low-temperature data $\rho_{i,0}$ and has a slope 95 ± 2 (V is excluded from the fit).

In order to test the functional form used in Fig. 1, we have used a nonlinear least-squares program to test more general forms for the high-temperature data. Again, only the data from cubic transition-metal host was used. Assuming the $\rho_{i,0} = \gamma\theta_D{}^\alpha/R^{\beta/2}$, we find that $\alpha = 1.00 \pm 0.09$, $\beta = 0.86 \pm 0.12$, and $\gamma = 136 \pm 76$. Using the form $\rho_{i,0} = \gamma\theta_D/R^{1/2} + \delta$ the parameters are $\delta = (0.24 \pm 0.55) \times 10^4$ and $\gamma = 128 \pm 11$. If the form chosen is $\rho_{i,0} = \gamma(\theta_D/\sqrt{R}) + \epsilon(\theta_D/\sqrt{R})^2$ we find $\gamma = 136 \pm 12$ and $\epsilon = 0.007 \pm 0.023$. In all fits $\rho_{i,0}$ are in temperature units. If the low-temperature data are fitted to $\rho_{i,0} = \gamma\theta_D/R^{1/2} + \delta$, we find $\gamma = 93 \pm 10$ and $\delta = (0.11 \pm 0.52) \times 10^4$.

The anomalously behaving V is the only system studied for which $R > 1$. It is the only case for which a virtual localized mode appears in the phonon continuum. V may also be anomalous because of a recently reported phase transition to a tetragonal lattice occurring at 230 K.[9]

The simple function form $\rho_{i,0} = \theta_D/\sqrt{R}$ is well verified. It is not the form expected from the model calculation presented above unless $K_h/K_i \sim R/(\theta_D)^{1/2}$. This result would follow from the assumption that the force constant for the impurity to the host is the geometric mean of the force constants for the impurity in bulk and for the host in bulk.[10]

We have searched for systematics of $\langle\omega\rangle_{i,0}$ and $\langle\omega^{-1}\rangle_{i,0}$ as well as their ratio. We have found no correlations with atomic radius differences, mass ratios, valancy, electronegativity, nor the Debye temperature of the host.

The existence of an unexpected and simple correlation of the McMillan phonon parameter $\langle\omega\rangle/\langle\omega^{-1}\rangle$ with the Debye temperature of the host and with R should provide an important clue to the nature of lattice dynamics of transition metals. The correlation is in disagreement with simple lattice dynamical theories, suggesting that the

scaling hypothesis used by McMillan and by Hopfield in their work on the theory of strong-coupling superconductors is questionable. Further theoretical work is required to convert these measurements into the McMillan parameter for the host atoms.

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Atomic and Molecular Diffraction of Helium and Deuterium from a Tungsten Carbide Surface Characterized by Low-Energy Electron Diffraction*

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The diffraction of thermal beams of helium and deuterium has been observed from a carbide overlayer on tungsten (110). The diffraction grating derived from the atomic and molecular diffraction agrees with that determined by electron diffraction. Peaks through second order have been resolved and helium peaks are characterized by extremely high intensities and narrow half-widths. Use of atomic diffraction to study species which adsorb in a regular array is suggested.

After the de Broglie postulate of the wave nature of matter in 1924, there were numerous attempts to observe the phenomenon experimentally via diffraction from a two-dimensional surface grating. In 1927 Davisson and Germer observed the diffraction of low-energy electrons which had been scattered from a single crystal of nickel.[1] In the early 1930's, Stern and co-workers observed the atomic and molecular diffraction of helium and hydrogen thermal beams from LiF and NaCl single crystals.[2-5] At the same time, Johnson observed the diffraction of a thermal beam of hydrogen atoms from LiF.[6] During the past forty years there have been many investigations of atomic and molecular diffraction from LiF in particular.[7-13] These workers have investigated the gas-surface interaction in both elastic-and inelastic-scattering events. Also there have been numerous attempts to observe atomic diffraction from other surfaces, notably metal surfaces (for a discussion see, e.g., Palmer, Saltsburg, and Smith[14] and Stoll and Merrill[15]) but none has been found except for the alkali halides, NaCl and LiF. In this Letter we report the diffraction of thermal He and D_2 beams from a W(110) surface with an overlayer carbide structure in a periodic (3×5) array rotated 35° with respect to the W substrate. The $R(3\times5)$ 35° was confirmed by low-energy electron diffraction (LEED). This carbide structure is similar to one previously reported on W(110) by Stern.[16]

The experimental apparatus has been described in detail previously[17]; very briefly it consists of a thermal molecular beam generated by an effusive source together with a LEED assembly in an ultrahigh-vacuum chamber (background pressure less than 7×10^{-11} Torr). Detection of either the direct beam or the scattered beam in the principal scattering plane is accomplished in the dc mode using a rotating probe connected to a stationary mass spectrometer. The angular resolution of the probe is approximately 2°. The