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Diffusion of H_2, D_2, and T_2 in Single-Crystal Ni and Cu[†]

L. Katz,[*] M. Guinan, and R. J. Borg
Lawrence Radiation Laboratory, University of California, Livermore, California 94550

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Diffusion coefficients have been obtained for H_2, D_2, and T_2 as a function of temperature in both Cu and Ni. The absolute-rate-theory formalism as proposed by Vineyard provides an adequate explanation of the results if quantum corrections and anharmonic effects are taken into consideration. The Ni results are especially affected by the failure of the harmonic approximation that apparently holds for Cu.

I. INTRODUCTION

A convenient and, in fact, customary starting point for a theoretical discussion of solid-state diffusion coefficients is Eq. (1), as provided by absolute-rate theory

$$D = f\nu^* e^{\Delta S^+/k} e^{-\Delta H^+/kT} \quad . \tag{1}$$

The symbols in this familiar equation are f, denoting the correlation coefficient; a hypothetical vibrational frequency ν^*; and ΔS^+ and ΔH^+, which are the entropy and enthalpy of activation and include values for the formation of lattice vacancies in the case of vacancy diffusion. There have been several theoretical attempts leading to relationships other than Eq. (1). However, it is probably safe to say that only absolute-rate theory has supplied a relationship readily amenable to experimental verification; consequently, it has provided the framework for most theoretical studies. Nevertheless, the validity of absolute-rate theory has been repeatedly challenged throughout its existence, and it has been difficult to conceive of experiments which provide unequivocal testimony. The apparent difficulties lie not so much with ΔS^+ and ΔH^+, which frequently can be measured by independent methods, but in visualizing the origin of ν^*. Over a decade ago, Vineyard[1] supplied a straightforward theoretical interpretation for ν^*; our experiments were largely aimed at verifying his model. To do this, we measured the diffusion coefficients for all three isotopes of hydrogen, for the mass dependence of ν^* as predicted by the Vineyard theory would seem to provide a critical test of theory.

There were three major reasons for selecting hydrogen as the diffusing species: First, the relative mass variation is the greatest of any element; second, we had three equally suitable isotopes rather than the customary two; and third, hydrogen diffuses interstitially. The third condition greatly simplifies the theoretical interpretation, since the correlation coefficient for interstitial diffusion is unity. The matrices, or host elements, Ni and Cu, were selected because of the relatively high solubility of hydrogen in them, and also because they are readily obtainable as high-purity single crystals. There are two previous investigations of the isotope effect in which H_2 and D_2 were employed. Eichenauer, Löser, and Witte[2] (ELW) measured diffusion coefficients in Ni and Cu, and concluded that their results were in accord with the predictions of simple rate theory. Ebisuzaki, Kass, and O'Keefe[3] (EKO) made additional measurements in Ni only, and by applying quantum-mechanical corrections, brought their results into better accord with theory. Our measurements both extend the temperature range and include an additional isotope, tritium. This additional information gives us a better insight into the theory and clearly points out the limitations of the previous interpretation. Two interesting "anomalies" observed by both ELW and EKO are clearly shown by our results: First, the measured values of D_α/D_β are much smaller than predicted by the simple relationship

$$D_\alpha/D_\beta = [M_\beta/M_\alpha]^{1/2}$$

in both Ni and Cu; and second, the ratio of the diffusion coefficients shows a substantial dependence upon temperature. An explanation of these observations will be presented in Sec. IV of this paper.

II. EXPERIMENTAL

The raw data are obtained by measuring the rate at which a specimen, initially saturated with hydrogen, outgasses. This method directly yields values for D, and offers a significant advantage over the permeation method, which yields only the product of the diffusion and solubility. In principle, one can also derive values for the solubility from the non-steady-state method, but the results in the present instance were erratic.

The metal specimens were spherical single crystals grown from 99.999% pure Ni and Cu. Although of initial high purity, the isotopes H_2 and D_2 were further purified by passing them over a charcoal-filled cold trap. The tritium was obtained from the decomposition of uranium tritide.

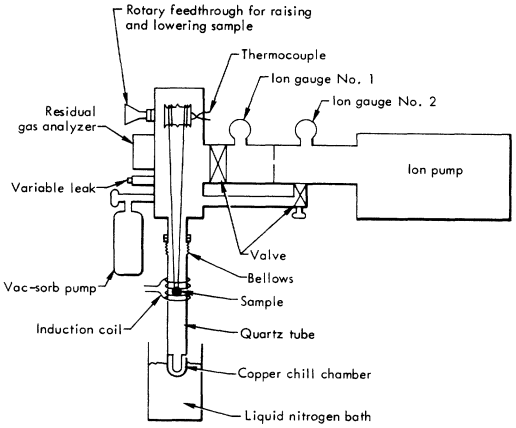

FIG. 1. A schematic diagram showing the essential features of experimental apparatus.

A high-vacuum diffusion apparatus as shown in Fig. 1 allows saturation of the specimen at an elevated temperature, followed by a quick thermal quench attained by quickly lowering it into a copper chill chamber maintained at liquid-nitrogen temperature. While the saturated sample remains in the chill chamber, the upper portion of the vacuum chamber is baked and pumped down to a background pressure of 10^{-7}–10^{-8} Torr. The specimen is then again raised into the hot zone and brought rapidly to the desired temperature by induction heating. The rise time required to achieve constant temperature is approximately 1 min, after which it remains constant to within ± 1 °C. The pressure of the evolving gas was measured with an ion gauge. The various isotopes were introduced successively into the system without opening it to the atmosphere. A mass spectrometer was initially incorporated into the system to determine the amount of any cross contamination between the various isotopes. However, the residual amount of the preceding isotope always proved to be less than the limit of the detection. Having thus been convinced that the degree of cross contamination was negligible, we permanently removed the mass spectrometer from the system.

The ion gauges located on both sides of the calibrated leak (see Fig. 1) provide the data necessary for the solution of Eq. (2)

$$dP/dt = Q_s + Q_b - Q_0 \ , \tag{2}$$

which states that the rate of change of the pressure is simply the difference between the flux of gas emitted by the specimen (Q_s), background outgassing (Q_b), and the flux through the orifice (Q_0). Neglecting the back pressure, the flow through an orifice is related to the pressure by the Knudsen relationship at low pressures, that is, Eq. (3),

$$Q_0 = \frac{PA}{22.4\times10^3}\left(\frac{2kT}{m}\right)^{1/2} , \tag{3}$$

where A is the area of the orifice and m is the molecular weight of the gas. The other symbols have their usual significance. The flux-out of the sample is given by Eq. (4)

$$Q_s = -\frac{d(\bar{C}V)}{dt} , \tag{4}$$

where $\bar{C}$ is the average concentration of gas within the sample and is related to the diffusion coefficient through Eq. (5), which is appropriate for diffusion out of a sphere

$$\frac{\bar{C} - C_i}{C_f - C_i} = 1 - \frac{6}{\pi^2}\sum_{\nu=1}^{\infty}\frac{1}{\nu^2}\, e^{-\nu^2\pi^2 Dt/r^2} . \tag{5}$$

In Eq. (5), $\bar{C}$, C_i, and C_f are the average, initial, and final concentrations; r is the radius of the sphere; and D and t have their usual meanings. At sufficiently long times, one can neglect all but the initial term in the summation and so obtain Eq. (6)

$$\frac{\bar{C} - C_i}{C_f - C_i} \cong 1 - \frac{6}{\pi^2}\, e^{-t/\tau} , \tag{6}$$

where $\tau = r^2/\pi^2 D$. Substituting for $\bar{C}$ in Eq. (4) and assuming $C_f \cong 0$, we obtain for Q_s,

$$Q_s \cong (6C_i/\pi^2\tau)\, e^{-t/\tau} . \tag{7}$$

We can now set

$$\alpha = 6C_0/\pi^2\tau, \quad \beta = [A/(2.24\times10^4)]\,(2kT/m)^{1/2} ,$$

$$Q_0 = \beta P_b .$$

By substituting into Eq. (2) and integrating, we arrive at Eq. (8)

$$P = \frac{\alpha}{\beta - 1/\tau}\, e^{-t/\tau} - \frac{\alpha}{\beta - 1/\tau}\, e^{-\beta t} + P_b , \tag{8}$$

where P_b, the background pressure, is usually about 5×10^{-7} Torr. A proper choice of orifice diameter causes the second term to decrease much more rapidly than the first; hence, at sufficiently long times, $\ln(P - P_b)$ vs t yields a linear plot from which the diffusion coefficient is directly calculable. A typical outgassing curve is shown in Fig. 2.

III. RESULTS

Our measurements in Cu extend from 450 to 925 °C, and in Ni from 400 to 1000 °C. These temperature ranges are more than twice as large as those of previous investigations[2,3] and, hence, allow a more accurate calculation of ΔH^*, the enthalpy of activation. In order to facilitate further analyses or comparisons by the interested reader, we have tabulated all the measured values in Table I. These same data are displayed graphically in Fig. 3. An unconstrained fit to the familiar Arrhenius relationship produced the values of ΔH^* and D^0 listed

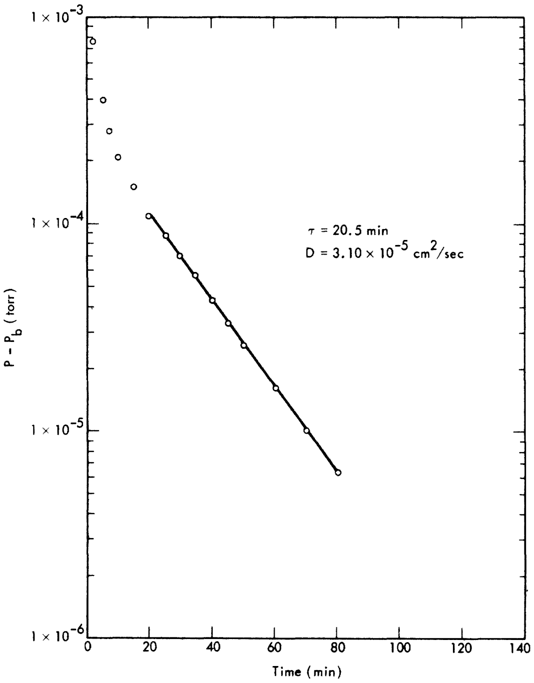

FIG. 2. A plot of the pressure difference across the orifice as a function of time. These data represent the rate of outgassing of H_2 from a single-crystal sphere of Ni at 600 °C. A value of D is calculated from the linear segment of the graph by applying Eq. (7).

in Table II. The error σ is simply the average deviation from the best straight line through all the data points. There is no measurable systematic departure from the Arrhenius relationship in any of the six systems investigated. As expected from previous investigations, both D^0 and ΔH^{+} decrease with increasing isotopic mass.

TABLE I. Measured diffusion coefficients.

T(°K)	D_1	D_2	D_3
		Ni	
673.2	6.15×10^{-6}	...	...
723	9.89×10^{-6}	8.26×10^{-6}	7.76×10^{-6}
773	1.50×10^{-5}	1.29×10^{-5}	1.16×10^{-5}
873	3.10×10^{-5}	2.62×10^{-5}	2.27×10^{-5}
973	5.35×10^{-5}	4.53×10^{-5}	3.84×10^{-5}
1123	9.93×10^{-5}	8.47×10^{-5}	7.11×10^{-5}
1198	1.37×10^{-4}	1.10×10^{-4}	9.37×10^{-5}
1273	1.71×10^{-4}	1.31×10^{-4}	1.23×10^{-4}
		Cu	
723	1.75×10^{-5}	1.64×10^{-5}	1.43×10^{-5}
773	2.72×10^{-5}	2.33×10^{-5}	2.12×10^{-5}
873	5.42×10^{-5}	4.73×10^{-5}	4.00×10^{-5}
973	9.18×10^{-5}	7.31×10^{-5}	6.54×10^{-5}
1073	1.42×10^{-4}	1.22×10^{-4}	1.06×10^{-4}
1173	2.13×10^{-4}	...	...
1198	2.32×10^{-4}	...	...

It is convenient to compare the diffusion coefficients of D and T to that of hydrogen in terms of Eq. (9)

$$D_{\mathrm{H}}/D_i = D^0_{\mathrm{H}}/D^0_i\, e^{-(\Delta H^{+}_{\mathrm{H}} - \Delta H^{+}_i)/RT} , \tag{9}$$

where the subscript i denotes either D or T. The pertinent values are given in Table II. It is noteworthy that $D^0_{\mathrm{H}}/D^0_i < (M_i/M_{\mathrm{H}})^{1/2}$ for Ni, but is larger in both cases for Cu.

IV. DISCUSSION

In terms of absolute-rate theory, we can consider the average jump frequency Γ for the diffusing atom to be given by the probability P_S that the system can reach a saddle surface (defined by maxima in the potential energy for any given diffusion path) times a frequency ν_D which corresponds to the rate at which the atom crosses this surface. P_S can be written as the ratio of a partition function Z_S for the system constrained to the saddle surface to the partition function Z for the total system. Thus, we can write

$$\Gamma = \nu_D Z_S / Z . \tag{10a}$$

For a harmonic system in the classical limit, this leads to Eq. (10b), a well-known expression[1] for the jump frequency

$$\Gamma^c = \left(\prod_{i=1}^{3N+3} \nu_i \Big/ \prod_{i=1}^{3N+2} \nu'_i \right) e^{-\Delta\phi^{+}/kT} . \tag{10b}$$

The products run over the $3N$ normal modes of the lattice plus the three additional modes of the

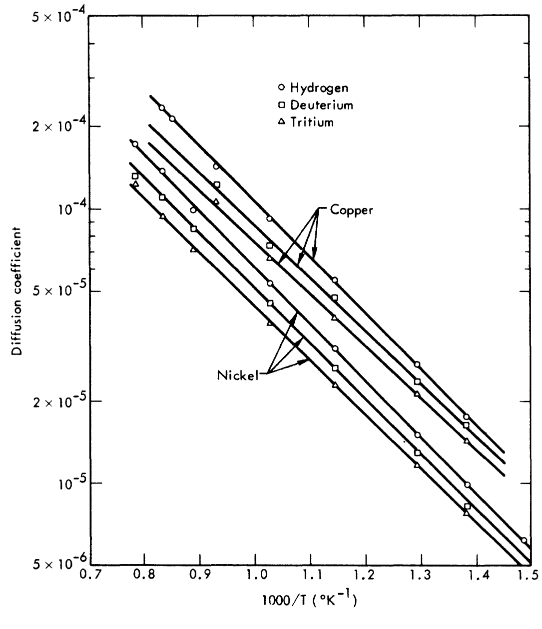

FIG. 3. Arrhenius plots for H_2, D_2, and T_2 diffusing in Cu (upper graphs) and Ni (lower graphs).

TABLE II. Separate Arrhenius fits to data.

	H	D	T
		Ni	
$10^3 D_0$(cm^2/sec)	7.04 ± 0.21	5.27 ± 0.28	4.32 ± 0.21
ΔH^+(cal)	9434 ± 52	9243 ± 96	9102 ± 87
σ	± 1.81%	± 2.73%	± 2.49%
		Cu	
$10^3 D_0$(cm^2/sec)	11.31 ± 0.40	7.30 ± 1.05	6.12 ± 0.51
ΔH^+(cal)	9286 ± 65	8794 ± 244	8717 ± 141
σ	± 1.72%	± 4.55%	± 2.62%

Ratios of diffusion coefficients in terms of D_0 and ΔH^+

		D_A^0/D_B^0	$\Delta H_A^+ - \Delta H_B^+$(cal)	Investigation
Ni	D_H/D_D	1.34	191	present
	D_H/D_D	1.41	270	ELW
	D_H/D_T	1.63	332	present
Cu	D_H/D_D	1.55	492	present
	D_H/D_D	1.85	710	ELW
	D_H/D_T	1.85	569	present

interstitial atom in its ground state or equilibrium configuration (EC), or the two additional modes when in the excited state. The excited state, of course, corresponds to the diffusing atom in the saddle-point configuration (SPC), which is at a potential $\Delta\phi^+$ above the potential in the equilibrium state. Equation (10b) was apparently first derived by Vineyard,[1] but only in its classical limit. More recently, several authors, beginning with Le Claire,[4] have done much to clarify the importance of the quantum-mechanical effects. EKO have taken them into account in their treatment of the diffusion of hydrogen in Ni, while Franklin[5] has also included anharmonic effects.

In its simplest, non-quantum-mechanical form, absolute-rate theory yields for the mass dependence of D the familiar result given by Eq. (11)

$$D_\alpha / D_\beta = \Gamma_\alpha^c / \Gamma_\beta^c = (M_\beta / M_\alpha)^{1/2} \ . \tag{11}$$

It will be instructive to review briefly the derivation of Eq. (11) if we are to ultimately understand why it fails, as it does, to coincide with the experimental values. The products of the normal-mode frequencies for both ground and excited states are given by Eqs. (12a) and (12b):

$$\prod_{j=1}^{3N+3} \nu_j = \frac{(\det \beta_{i,j})^{1/2}}{(2\pi)^{3N+3}} \prod_{j=1}^{3N+3} \frac{1}{(M_j)^{1/2}} \ , \tag{12a}$$

$$\prod_{j=1}^{3N+2} \nu_j' = \frac{(\det \beta_{ij}')^{1/2}}{(2\pi)^{3N+2}} \prod_{j=1}^{3N+2} \frac{1}{(M_j')^{1/2}} \ . \tag{12b}$$

Hence, we can write for the jump frequency

$$\Gamma = \frac{(\det \beta_{ij})^{1/2}}{(\det \beta_{ij}')^{1/2}} \left(\prod_{j=1}^{3N+3} M_j^{-1/2} \Big/ \prod_{j=1}^{3N+2} M_j'^{-1/2} \right) e^{-\Delta\phi^+/kT} \ .$$

By making use of the product rule, we have

$$\Gamma = \left[\frac{\det \beta_{ij}}{\det \beta_{ij}'} \right]^{1/2} \frac{1}{M^{1/2}} e^{-\Delta\phi^+/kT} \ , \tag{13}$$

where M is the mass associated with the transition mode. Since the force constants β_{ij} and β_{ij}' are mass-independent quantities, we can immediately obtain Eq. (11) by simply writing the quotient of two equations such as Eq. (13) for each of two different isotopic masses if the assumption is made that M is the mass of the diffusing atom.

The isotopic variation of the diffusion coefficient for several chemically diverse systems conforms quite accurately to Eq. (11)—for example, self-diffusion [6,7] in Pd and in Ag as well as the diffusion[8] of Na in NaCl and C in Fe.[9] However, significant departure from the square-root relationship has been observed previously for systems other than those reported here, e.g., the diffusion[10] of ^{65}Zn and ^{69}Zn in CuZn, or the diffusion[11] of ^{55}Fe and ^{59}Fe in Fe-Si alloys.

Within the framework of absolute-rate theory, departures from Eq. (11) can arise from the neglect of several effects: (i) velocity correlation (ΔK effect); (ii) quantum effects (Böse statistics and tunneling); (iii) anharmonicity.

In the cases cited above, the discrepancy has been attributed to the so-called ΔK effect, which we will consider next, with particular reference to the diffusion of hydrogen.

A. ΔK Effect

In deriving Eq. (11) from Eq. (13), we had previously assumed that the mode mass M was equal to the mass of the diffusing atom. In order to explain the ΔK effect, it is necessary to remove this assumption. For the sake of simplicity, though, we continue to treat the entire system as *coupled classical harmonic oscillators*, ignoring for the moment any possible quantum effects. The relationship which defines the isotope effect, viz., Eq. (14), was first derived by Mullen[12] and also serves to define ΔK in terms of measurable parameters

$$\Gamma_\alpha / \Gamma_\beta - 1 = \Delta K [(M_\alpha / M_\beta)^{1/2} - 1] \ . \tag{14}$$

Following Vineyard's treatment, Mullen finds that ΔK is the ratio of the kinetic energy carried by the diffusing atom in the transition mode to the total kinetic energy associated with this mode; hence, the notation ΔK. Unfortunately, the source of the effect is somewhat obscured by the use of mass-weighted normal coordinates.

LeClaire,[4] also using mass-weighted normal coordinates, has provided additional insight into the source of the effect by relating ΔK to the atomic displacements involved in the transition mode. His expression for ΔK (valid for small relative changes in isotopic mass) was shown to be equivalent to that derived by Mullen.

Glyde[13] has demonstrated that the mass M in Eq. (13) will be that of the diffusing species, as long as there is no correlation between the velocities of different atoms. Such correlations, for example, could arise from resonance modes, in the case of a diffusing atom that was substantially heavier than the matrix, or from lattice strains associated with the diffusing species.

If the diffusing atom is completely decoupled, or "there exists no lattice strain," then ΔK is unity and Eq. (11) is restored. However, a more exact analysis must take into account the strain field which accompanies the interstitial atom (or vacancy, as the case may be). If one now correctly accounts for the total displacement of both matrix and the interstitial atom, ΔK is no longer unity, which is another way of saying that the mass dependence must reflect the *total* displacement of mass.

In a yet more recent derivation (valid for any mass substitution), Glyde[14] avoids the use of mass-weighted normal coordinates entirely and obtains Eq. (15), which is more directly applicable to the data,

$$\frac{\Gamma_\alpha}{\Gamma_\beta}=\frac{M_\beta^{1/2}}{M_\alpha^{1/2}}\left[1+\frac{M_\alpha}{M}\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2\right]^{1/2}\Bigg/\left[1+\frac{M_\beta}{M}\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2\right]^{1/2} . \quad (15)$$

In Eq. (15), d_{1p} is the normalized displacement of the diffusing atom along the transition normal coordinate p, d_{ip} is the normalized displacement of atom i along p, and M is the mass of the host atoms. It is clear that, were the displacements of the lattice atoms null, the terms in brackets would reduce to unity, yielding Eq. (11) once again. It is also obvious that when $M_\alpha < M_\beta$, the entire second term on the right-hand side must be less than unity and hence, in such a case, the ΔK *effect can only reduce the predicted value of* D_α/D_β. In order to demonstrate the failure of the ΔK effect to explain the Ni results, it is necessary to explicitly calculate $\sum(d_{ip}/d_{1p})^2$, which is estimated in Appendix A. However, the value thus calculated, viz., Eq. (A6), leads to a correction on the order of a few tenths of 1%. Consequently, we can discard the ΔK effect as a possible explanation of the departure of our results from Eq. (11).

B. Quantum Effects

Let us next examine the consequences of having used classical rather than the more correct quantum vibrational partition functions in deriving Eq. (11). This indeed is quite likely to be a poor approximation for the diffusion of atoms as light as hydrogen in metals, since the vibrational level separations are expected to be of the order of $\frac{1}{10}$ eV.

Quantum effects in the harmonic approximation have been treated by LeClaire,[4] Ebisuzaki *et al.*,[3] and Franklin.[5] All began by using the quantized harmonic-oscillator partition functions for Z and Z_S in Eq. (10a). Their approaches differed only in their treatment of ν_D. For the moment, we will ignore any quantum effects arising from ν_D, taking the classical limit kT/h.

In his treatment, LeClaire[4] expands the partition functions in a power series in $h\nu/kT$, retaining only the first two terms. It has been subsequently shown by EKO[15] that two terms alone are probably inadequate to describe the experimental results over their temperature range. We will follow them by retaining all terms and deriving the quantum-mechanical analog to Eq. (11) with two additional approximations. First, the vibrational modes of the hydrogen are once again assumed to be completely decoupled from the lattice modes. Second, because the highest lattice frequencies of Ni and Cu are ~ 9×10^{12} and ~ 7.5×10^{12} Hz, respectively, as determined by neutron diffraction, we may safely employ classical partition functions to describe the lattice modes, i.e., within the temperature range of interest, $h\nu/2kT \leq \frac{1}{2}$ (the error attendant upon this approximation is less than 1% and will be much reduced when the ratio of two coefficients is taken). Making use of these approximations, we rewrite Eq. (10a) as follows:

$$\Gamma=\left(\prod_{i=1}^{3N+3}\nu_i\Big/\prod_{i=1}^{3N+2}\nu_i'\right)e^{-\Delta\phi^+/kT}\times\left(\prod_{i=1}^{3}\frac{\sinh(h\nu_i/2kT)}{h\nu_i/2kT}\Big/\prod_{i=1}^{2}\frac{\sinh(h\nu_i'/2kT)}{h\nu_i'/2kT}\right) . \quad (16)$$

With the additional assumption that the local-mode distribution is isotropic, Eq. (16) finally reduces to Eq. (17)

$$\Gamma=\Gamma^c\left(\frac{\sinh(h\nu/2kT)}{h\nu/2kT}\right)^3\Bigg/\left(\frac{\sinh(h\nu'/2kT)}{h\nu'/2kT}\right)^2 , \quad (17)$$

where Γ^c is given by Eq. (10b).

Setting $\theta = h\nu/k$ and $\theta' = h\nu'/k$, and letting $f_\alpha = \sinh(\theta/2\alpha^{1/2}T)/(\theta/2\alpha^{1/2}T)$ and $f_\alpha' = \sinh(\theta'/2\alpha^{1/2}T)/(\theta'/2\alpha^{1/2}T)$, we obtain the same equation as EKO for the ratio of the diffusion coefficients

$$\frac{D_\alpha}{D_\beta}=\left(\frac{\beta}{\alpha}\right)^{1/2}\frac{f_\alpha^3 f_\beta'^2}{f_\beta^3 f_\alpha'^2} , \quad (18)$$

where, as before, $\alpha, \beta = 1, 2, 3$ for H, D, T, respectively. Because we now possess diffusion data for tritium as well as hydrogen and deuterium, we can solve Eq. (18) for the first time without resort to solubility data.

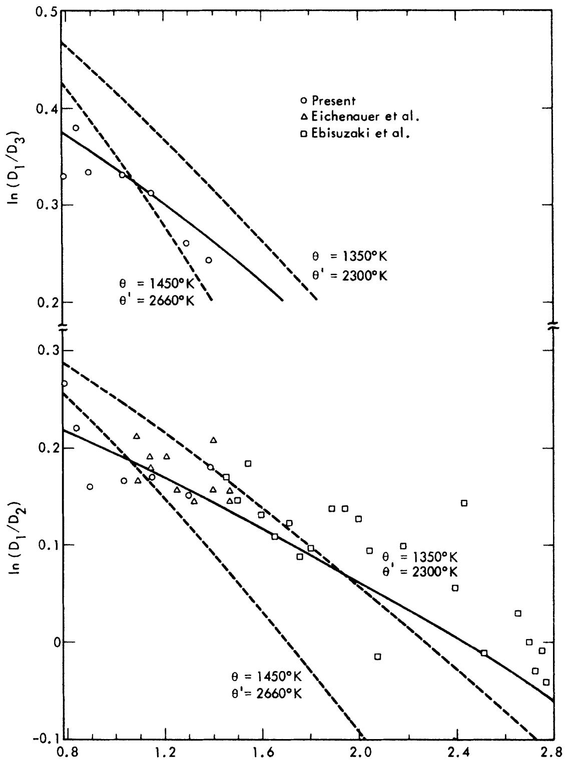

FIG. 4. All available diffusion ratios of [H]/[D] and [H]/[T] as functions of temperature in Ni. The dotted lines are the predictions of the harmonic theory. The solid line is calculated from the anharmonic theory.

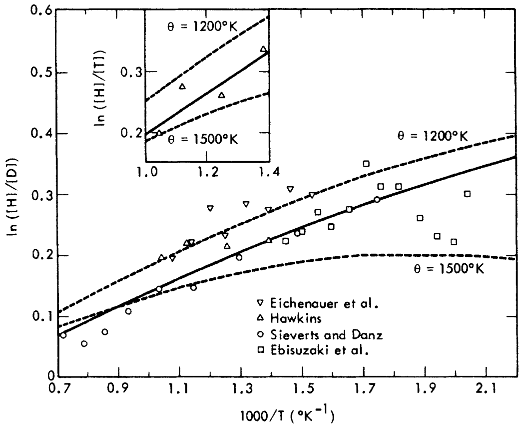

FIG. 5. All available solubility ratios of [H]/[D] and [H]/[T] as functions of temperature in Ni. The dotted lines are the predictions of the harmonic theory for the values of θ indicated. The solid line is calculated from the anharmonic theory (see text).

Equation (18) provides a good fit to the experimentally determined ratios over the entire temperature range, using the values of θ and θ' listed below:

Ni $\theta_{\mathrm{Ni}} = 3830$ °K , $\theta'_{\mathrm{Ni}} = 5480$ °K ,

Cu $\theta_{\mathrm{Cu}} = 1740$ °K , $\theta'_{\mathrm{Cu}} = 2980$ °K .

It is clearly apparent that the values for Ni are so large as to be physically unrealistic, whereas those for Cu appear acceptable. By way of comparison EKO,[3] using solubility as well as diffusion data for H_2 and D_2 only, calculate $\theta_{\mathrm{Ni}} = 1350$ °K and $\theta'_{\mathrm{Ni}} = 2300$ °K. These values give a poor although acceptable fit to our measured values of $D_{\mathrm{H}}/D_{\mathrm{D}}$, but completely fail to fit our values of $D_{\mathrm{H}}/D_{\mathrm{T}}$ (see Fig. 4).

TABLE III. Values of θ derived from Eq. (19).

Isotopic ratio	θ (°K) Ni	Reference
[H]/[D]	1150	2
[H]/[D]	1350	3
[H]/[D]	1280	14
[H]/[T]	1390	14
[H]/[D]	1400	15
	θ (°K) Cu	
[H]/[D]	1600	2

In principle, both neutron scattering[16] as well as solubility measurements can provide the means of independently calculating θ; unfortunately, the neutron scattering experiments have yet to be performed. However, there are several pertinent solubility studies for Ni[2,3,17] and at least one for Cu.[2] The solubility ratio $[\alpha]/[\beta]$ is related to θ through the following equation (see Appendix B):

$$\ln\frac{[\alpha]}{[\beta]} = 3\ln\left[\frac{f_\beta}{f_\alpha}\right] - \frac{3}{2}\ln\left(\frac{M_\beta}{M_\alpha}\right) + \frac{G^0_\alpha - G^0_\beta}{2RT} . \qquad (19)$$

The values of θ derived from Eq. (19) are listed in Table III. It is apparent that there is no agreement whatsoever between the values of θ_{Ni} derived from solubility and those derived here solely from diffusion, the latter being about three times larger than the former. On the other hand, θ_{Cu} is in reasonable agreement.

We have compared all the reliable solubility data with Eq. (19), and the results are shown graphically in Figs. 5 and 6 for Ni and Cu, respectively, with the ratio [H] / [D] plotted as ln([H] / [D]) vs T^{-1}. The dotted lines derive from Eq. (19) for the indicated values of θ, and it is clear that a majority of the measured values for Ni fall between 1200 °K $\leq \theta_{\mathrm{Ni}} \leq 1500$ °K, while those for Cu fall between 1400 and 1700 °K. Except at the lowest temperatures, the best fits are obtained with $\theta_{\mathrm{Ni}} = 1350$ °K, and $\theta_{\mathrm{Cu}} = 1600$ °K. Based solely on the precision of

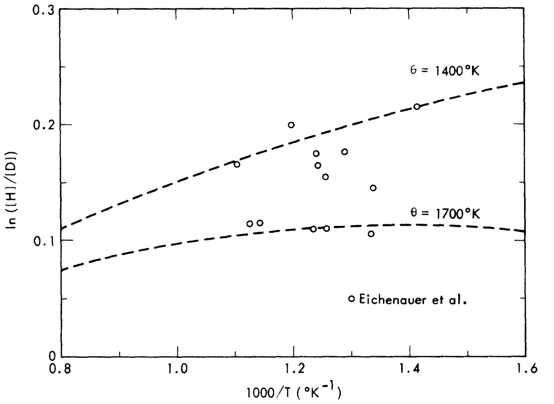

FIG. 6. Available solubility ratio [H]/[D] in Cu as a function of temperature. The dotted lines are the predictions of the harmonic theory for the values of θ indicated.

the fit, we would assign error limits of ± 50 °K to the preceding values.

Using the values of θ derived from solubility, we can, from Eq. (18), obtain $\theta'_{\mathrm{Ni}} = 2620$ °K and $\theta'_{\mathrm{Cu}} = 2850$ °K from a single adjustable parameter fit to $D_{\mathrm{H}}/D_{\mathrm{D}}$ and $D_{\mathrm{H}}/D_{\mathrm{T}}$. These values for θ'_{Ni} and θ'_{Cu} reproduce the average values of the ratios at the midrange of T^{-1} for both Cu and Ni, but give consistently higher slopes than the measurements for Ni, as shown in Figs. 4 and 7. Except for the consistently greater slope for Ni, the fit is within the experimental limits of error of our measurements. However, the results of EKO[3] for Ni extend to much lower temperatures than do ours and lie several standard deviations away from those predicted. In summary, Eq. (18) provides a very poor approximation over the entire range for which measurements exist in Ni, so poor in fact as to be regarded as a complete failure.

In addition to the quantum corrections arising from the vibrational partition functions, we should also consider those arising from ν_D. While the possibility exists that hydrogen transport in Ni, like that in the bcc metals, is essentially a quantum phenomenon, both heuristic arguments,[3] as well as a full-scale quantum-mechanical band-model treatment by Lepski,[18] lead to the conclusion that tunneling will not be the dominant transport mechanism in fcc metals at these temperatures.

Quantum corrections to ν_D can arise from two sources. First, the level spacings of the partially bound diffusing atom are coarse with respect to both kT and $\Delta\phi^{+}$. This effect will be present apart from any tunneling and has been considered by Franklin,[5] who writes ν_D as the ratio of the rms velocity in the diffusion direction to the deBroglie wavelength, $\lambda = h/(MkT)^{1/2}$. Thus, for the isotropic local modes considered here, we obtain

$$\nu_{D_\alpha} = \frac{kT}{h}\left[\frac{\theta}{2(\sqrt{\alpha})T}\coth\left(\frac{\theta}{2(\sqrt{\alpha})T}\right)\right]^{1/2}, \qquad (20a)$$

which reduces to the classical value kT/h for $T \gg \theta$.

A plausible alternative to Franklin's expression for ν_D is to associate ν_D with the mean energy of the diffusing mass through the Einstein relation—i.e., $\nu_D = \langle E\rangle/h$. In this case, we have

$$\nu_{D_\alpha} = \frac{kT}{h}\left[\frac{\theta}{2(\sqrt{\alpha})T}\coth\left(\frac{\theta}{2(\sqrt{\alpha})T}\right)\right], \qquad (20b)$$

a correction about twice as large as that given by Franklin.

Following EKO,[3] one can take tunneling into account by multiplying Eq. (17) by a "tunneling correction factor" $(f^{+})^{-1}$ given by

$$(f_\alpha^{+})^{-1} = \frac{\theta^{+}}{2(\sqrt{\alpha})T} \Big/ \sin\left(\frac{\theta^{+}}{2(\sqrt{\alpha})T}\right), \qquad (20c)$$

where $\theta^{+} = h\nu^{+}/kT$, and ν^{+} is related to the mass of the diffusing atom and the curvature of the potential along the transition coordinate at the saddle point in the usual manner. EKO[3] argued on geometrical grounds that ν^{+} was so small that any correction arising from Eq. (20c) is negligible. A simple estimate based on the screened proton model for H in Ni indicated that $\theta^{+} \sim 0.4\,\theta'$. Although the re-

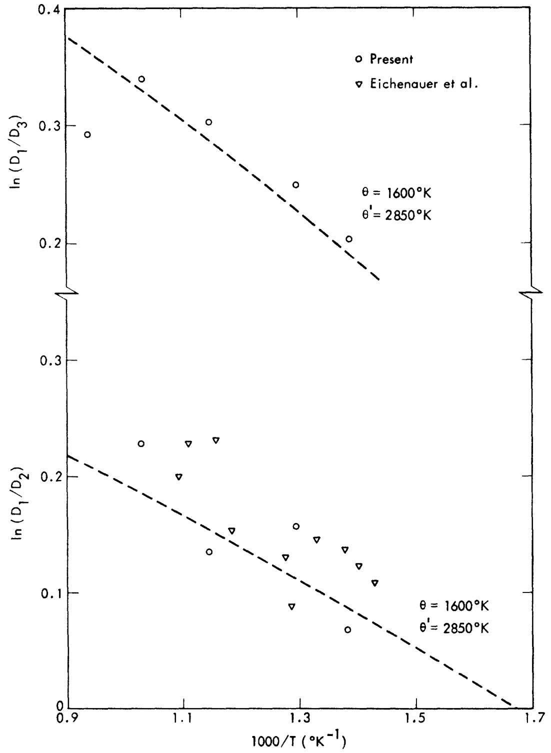

FIG. 7. All available diffusion ratios [H]/[D] and [H]/[T] as functions of temperature in Cu. The dotted lines are the predictions of the harmonic theory.

sulting correction is small in comparison to the other quantum corrections, it is not entirely negligible.

If we write f''_α for the square bracket in Eq. (20b), then we obtain the jump frequency of isotope α

$$\Gamma_\alpha = \Gamma^c_\alpha (f_\alpha)^3 (f'_\alpha)^{-2} (f''_\alpha)(f^+_\alpha)^{-1} , \tag{21a}$$

as a product of the classical jump frequency times appropriate powers of four quantum correction factors. For convenience, the four factors and their series expansions are written below:

$$f_\alpha = \left(\frac{\theta}{2(\sqrt{\alpha})T}\right)^{-1} \sinh\frac{\theta}{2(\sqrt{\alpha})T} = 1 + \frac{1}{24\alpha}\left(\frac{\theta}{T}\right)^2 + \frac{1}{1920\alpha^2}\left(\frac{\theta}{T}\right)^4 + \cdots , \tag{21b}$$

$$f'_\alpha = \left(\frac{\theta'}{2(\sqrt{\alpha})T}\right)^{-1} \sinh\frac{\theta'}{2(\sqrt{\alpha})T} = 1 + \frac{1}{24\alpha}\left(\frac{\theta'}{T}\right)^2 + \frac{1}{1920\alpha^2}\left(\frac{\theta'}{T}\right)^4 + \cdots , \tag{21c}$$

$$f''_\alpha = \left(\frac{\theta}{2(\sqrt{\alpha})T}\right) \coth\frac{\theta}{2(\sqrt{\alpha})T} = 1 + \frac{1}{12\alpha}\left(\frac{\theta}{T}\right)^2 - \frac{1}{720\alpha^2}\left(\frac{\theta}{T}\right)^4 + \cdots , \tag{21d}$$

$$f^+_\alpha = \left(\frac{\theta^+}{2(\sqrt{\alpha})T}\right)^{-1} \sin\frac{\theta^+}{2(\sqrt{\alpha})T} = 1 - \frac{1}{24\alpha}\left(\frac{\theta^+}{T}\right)^2 + \frac{1}{1920\alpha^2}\left(\frac{\theta^+}{T}\right)^4 - \cdots . \tag{21e}$$

The inclusion of these corrections cannot, however, resolve the disagreement between theory and experiment for Ni. Over the temperature range covered by experiments, only the terms quadratic in $1/T$ make any significant contribution to the values of the correction factors. Thus the inclusion of f'' and f^+ will not significantly modify the temperature dependence of the theory.

C. Anharmonic Corrections

We can successfully fit the data with absolute-rate theory only if we assume that θ' increases with increasing temperature. This is perhaps a reasonable assumption in view of the fact that even the value of θ_{Ni} derived strictly from the solubility data (see Fig. 5) appears to increase with temperature. For example, using Eq. (19) and the data of Sieverts and Danz,[19] we calculate $\theta_{\mathrm{Ni}} = 1350$ °K at 650 °K and $\theta_{\mathrm{Ni}} = 1450$ °K at 950 °K, an increase of 100 °K within a 300 °K interval. The first value corresponds to the midrange temperature of the diffusion measurements of EKO,[3] and the last corresponds to the midrange of our measurements. Taking these values, as well as the measured values of the diffusion coefficients, we calculate, by means of Eq. (18), from EKO[3]

$$\theta_{\mathrm{Ni}} = 1350\ \text{°K} , \quad \theta'_{\mathrm{Ni}} = 2300\ \text{°K at } 650\ \text{°K} ,$$

and from present work,

$$\theta_{\mathrm{Ni}} = 1450\ \text{°K} , \quad \theta'_{\mathrm{Ni}} = 2660\ \text{°K at } 950\ \text{°K} ,$$

which illustrates the magnitude of the response of θ'_{Ni} to the variation in θ_{Ni}.

In the derivation of Eq. (18), explicit assumptions were made concerning the vibrational properties of the hydrogen, viz., that there are no long-range H-H or H-Ni interactions and that as a consequence the local-mode approximation obtains. Also, it was assumed that the vibrational energy levels are adequately described by a quantum-mechanical *harmonic* oscillator. The first assumption would appear to be valid in view of the dilute hydrogen concentration and the large gap in the H-Ni frequencies. The second assumption may not in fact be justified, and failure of the hydrogen to behave as a simple harmonic oscillator can account for the apparent failure of classical rate theory.

We will now examine the consequences of removing the restriction of harmonicity.

The first nonvanishing correction to the energy levels of a quantum-mechanical oscillator in a symmetric one-dimensional potential well is given by Eq. (22)

$$E_n = E_0 + h\nu_0(n+\tfrac{1}{2}) + (C/16K^2)(h\nu_0)^2[(n+\tfrac{1}{2})^2 + \tfrac{1}{4}] , \tag{22}$$

where $\nu_0^2 = K/4\pi^2 m$, the m being the mass of the oscillator, and K and C being the first two coefficients in the expansion of the potential

$$U = U_0 + \frac{K}{2!}(\Delta X)^2 + \frac{C}{4!}(\Delta X)^4 . \tag{23}$$

In order to explain the large temperature dependence, the energy difference between the first two level spacings would have to vary by (10–20)%; the question is now whether such a large anharmonic effect is justified for H_2 in Ni. We will attempt to make just such a justification on the basis of estimates derived from the screened-proton model that appears to at least qualitatively account for the solubility.[20]

Equation (24) gives the energy of the repulsive interaction of the Ni ion core with the screened proton

$$E_{\mathrm{rep}} = (A/r)e^{-\lambda r} , \tag{24}$$

where λ is the proton screening parameter, and r the proton-ion core separation. The constant A can, in principle, be determined from the nickel pseudopotential.[21] To conform with Eq. (23), we will expand Eq. (24) for hydrogen in an octahedral site

$$E(r)=E(r_0)\left(1+\frac{1}{2!}\,\frac{\lambda^2}{4}\,(\Delta x^2+\Delta y^2+\Delta z^2)+\frac{1}{4!}\,\frac{\lambda^4}{3}\,(\Delta x^4+\Delta y^4+\Delta z^4)\right), \quad (25)$$

where r_0 is the equilibrium proton-nickel separation.

In Eq. (25), we have retained only the highest power of λr_0 in each order, since for Ni we expect $\lambda r_0 \simeq 12$. We have also neglected a term in Δr^4 whose coefficient is small compared to that of $\Delta x^4+\Delta y^4+\Delta z^4$. In this approximation then, we have three independent linear oscillators. Comparing Eq. (25) with Eq. (22) we have

$$K=\tfrac{1}{3}\lambda^2 E(r_0)\,, \quad C=\tfrac{1}{3}\lambda^4 E(r_0)\,. \quad (26)$$

A similar expansion assuming a $\langle 111\rangle$ saddle point, i.e., midway between the octahedral and tetrahedral site, leads to

$$K'=\tfrac{1}{2}\lambda^2 E'(r_0')\,, \quad C'=\tfrac{3}{8}\lambda^4 E'(r_0')\,. \quad (27)$$

In this case, however, C' is the coefficient of Δr^4, and the energy levels for both saddle-point oscillations will be given in Eq. (28) (see Ref. 22)

$$E_{n,m}=E_s+h\nu_0'(n+1)+(C'/16K'^2)(h\nu_0')^2 \times\left[(n+1)^2+\tfrac{1}{3}-\tfrac{1}{3}m^2\right], \quad (28)$$

where $\pm m=n,\ n-2,\ n-4,\ \ldots,\ 0$ or 1.

We now need to correct the harmonic-oscillator partition functions for the anharmonic terms. In Appendix C, we show that in terms of the function $f_\alpha=\sinh(u/2\sqrt{\alpha})/(u/2\sqrt{\alpha})$ we can write

$$\frac{1}{f_{A_\alpha}}=\frac{1}{f_\alpha}\left(1-\frac{2xu}{u^2}\,\frac{1}{f_\alpha^2}\right)e^{-xu/2\alpha}\,, \quad (29)$$

where $u=h\nu_0/kT=\theta/T$, and $\nu_0=(K/4\pi^2M)^{1/2}$ is the frequency of the unperturbed harmonic oscillator.

The calculated solubility and diffusivity ratios can be corrected for anharmonic effects by substituting f_A [from Eq. (29)] for f in Eqs. (19) and (21a), respectively. For the solubility, we obtain, making the obvious substitutions and using $\ln(1+\Delta)\cong\Delta$,

$$\ln\frac{[\alpha]}{[\beta]}=\ln\frac{[\alpha]}{[\beta]}\bigg|_{\mathrm{H}}-\frac{3}{2}\,\frac{\phi}{T}\left(\frac{1}{\alpha}-\frac{1}{\beta}\right)+6\,\frac{\phi}{T}\,\frac{1}{u^2}\left(\frac{1}{f_\beta^2}-\frac{1}{f_\alpha^2}\right) \quad (30)$$

with

$$\phi=\hbar^2C/16kKm_{\mathrm{H}}\,,$$

where

$$m_{\mathrm{H}}=\text{hydrogen mass}\,,\quad k=\text{Boltzmann constant}. \quad (31)$$

At high temperatures (i.e., $T\geq\theta$), the last term in Eq. (30) can be evaluated by expanding f_α and f_β (e.g., $f_\alpha=1+(1/\alpha)(u^2/24)+\cdots$), giving $\frac{1}{2}(\phi/T)\times(1/\alpha-1/\beta)$. At low temperatures the last term vanishes. Thus, the anharmonic correction depends only on ϕ, varying from $-(\phi/T)(1/\alpha-1/\beta)$ at high temperatures to $-\frac{3}{2}(\phi/T)(1/\alpha-1/\beta)$ at low temperatures.

Substituting the values of C, C', K, and K' from Eqs. (26) and (27), we have

$$\phi=\hbar^2\lambda^2/16km_{\mathrm{H}}\,,\quad \phi'=\tfrac{3}{4}\phi\,. \quad (32)$$

Using primes to denote quantities associated with the saddle-point configuration, making use of Eq. (29) and the modification for the saddle point given in Appendix C, we obtain, for the diffusivity ratio,

$$\ln\frac{D_\alpha}{D_\beta}=\ln\frac{D_\alpha}{D_\beta}\bigg|_{\mathrm{H}}+\left[\left(\frac{3}{2}\phi-\frac{4}{3}\phi'\right)\frac{1}{T}\right]\left(\frac{1}{\alpha}-\frac{1}{\beta}\right)-6\,\frac{\phi}{T}\,\frac{1}{u^2}\left[\left(\frac{1}{f_\beta}\right)^2-\left(\frac{1}{f_\alpha}\right)^2\right]+4\,\frac{\phi'}{T}\,\frac{1}{u^2}\left[\left(\frac{1}{f_\beta'}\right)^2-\left(\frac{1}{f_\alpha'}\right)^2\right]. \quad (33)$$

Proceeding as before, the correction will be approximately $[-(\phi'-\phi)/T](1/\alpha-1/\beta)$ at high temperatures and $-(\frac{4}{3}\phi'-\frac{3}{2}\phi)(1/T)(1/\alpha-1/\beta)$ at low temperatures.

Thus, the anharmonic corrections depend only on the screening parameter λ given approximately by[20,23]

$$\lambda_0^2=4\pi e^2N_0\,, \quad (34)$$

where N_0 is the density of states at the Fermi level. If N_0 is estimated on a free-electron model from the low-temperature electronic specific heat, then $\lambda_0=7.2$ Å^{-1} for Ni, and $\lambda_0=2.2$ Å^{-1} for Cu.[20] Substituting these values in Eq. (32), we find that $\phi=156$ °K for Ni, and $\phi=16$ °K for Cu.

D. Comparison with Experiment

Using a value of $\phi=160$ °K and $\theta=920$ °K, one can make a reasonable fit to all the available solubility data for Ni, producing the solid curve in Fig. 5.

Whereas θ and ϕ are measurable physical properties of the system, θ', θ^* and ϕ' have meaning only through their relation to the derivatives of the potential at the saddle point, and must be inferred from experiment or calculated from a suitable model. Using the simple model developed above, we expect $\theta'\sim3\theta$ and $\theta^*\sim0.4\theta'$. An estimate of relaxations around the hydrogen will reduce both values to $\theta'\sim2\theta$ and $\theta^*\sim0.35\theta'$. Thus θ^* would appear to be small enough so that $f^*\sim1$ over the temperature range of interest.

Using $\theta = 920\ ^\circ\mathrm{K}$, $\phi = 160\ ^\circ\mathrm{K}$, and $\theta^* = \frac{1}{3}\theta'$, the theory expressed by Eq. (33) was fit to our data by adjusting θ' and ϕ'. A good fit is obtained for $\theta' = 2100\ ^\circ\mathrm{K}$ and $\phi' = 340\ ^\circ\mathrm{K}$. The result shown in Fig. 6 is a substantial improvement over the harmonic theory. Although θ' is about as expected, ϕ' is nearly three times as large as the predicted value of 120 °K.

The relative success of the simple model presented here in accounting for the mass dependence of hydrogen diffusion in Ni and Cu would indicate that a direct calculation of the diffusion coefficient may be possible, for example, through the formalism developed by Franklin. [5]

No attempt has been made to adjust the Cu fit, since the corrections are well within the experimental uncertainties.

We note that the value of $\theta = 920\ ^\circ\mathrm{K}$ will not correspond to a measurable local-mode frequency, since it corresponds to a hypothetical harmonic oscillator. Neutron diffraction measurements would, for example, measure the first actual level spacing, i.e., $\theta + 2\phi = 1230\ ^\circ\mathrm{K}$. Commenting on this aspect, we might also note that the measurement of higher harmonics should allow a determination at both θ and ϕ.

V. SUMMARY

Absolute-rate theory in its proper quantum-mechanical form provides an acceptable description for the diffusion of hydrogen in Cu, but apparently fails for Ni. Arguments are provided that attribute this seeming failure not to absolute-rate theory *per se*, but to the harmonic approximation, which is universally employed. This approximation holds for the diffusion of hydrogen in Cu, but not in Ni, which is consistent with the difference in the screening parameter. It is obvious that the inclusion of anharmonic terms improves the fit between theory and experiment, although the detailed knowledge of the H-Ni interaction necessary to make the results exact is self-evidently lacking. It is postulated that the harmonic approximation will prove inadequate for all close-packed metal systems in which the density of states at the Fermi surface is comparable to that of Ni.

It is noteworthy that all three isotopes of hydrogen were necessary in order to reveal the discrepancy between theory and experiment. If one calculates θ and θ' using diffusion data for but two isotopes, for example, H_2 and D_2, this yields in combination with solubility data an acceptable fit for the selfsame two isotopes, but not, as we have shown, for the third. It is consequently necessary to obtain data on all three isotopes in order to reveal the suitability of the harmonic approximation.

It is apparent that neither the ΔK effect nor tunneling can have a detectable influence upon the diffusion. The latter phenomenon may, of course, become significant at temperatures much below those of this investigation.

APPENDIX A

The displacement resulting from a point source of expansion (e.g., a hydrogen atom) is given by[24]

$$\vec{U} = (\delta v / 4\pi r^3)\,\vec{r}\ , \tag{A1}$$

where δv is the source strength.

If we displace the source by $\Delta\vec{r}$, the displacement becomes

$$\vec{U}' = (\delta v / 4\pi r'^3)\,\vec{r}'\ , \tag{A2}$$

where $\vec{r}' = \vec{r} - \Delta\vec{r}$. The resulting displacement of surrounding material is thus

$$\vec{d} = \vec{u}' - \vec{u}\ . \tag{A3}$$

The relative displacements appearing in Eq. (16) are thus

$$\frac{d_{ip}}{d_{1p}} = \frac{\vec{d}\cdot\Delta\vec{r}}{(\Delta r)^2}\ , \tag{A4}$$

and we can write

$$\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2 = \int_{r_0}^{\infty}\left(\frac{\vec{d}\cdot\Delta\vec{r}}{\Delta r^2}\right)^2\frac{dV}{V_A}\ , \tag{A5}$$

where V_A is the atomic volume.

Using spherical coordinates with $\Delta\vec{r}$ along z and making use of Eqs. (A1)–(A4), Eq. (A5) can be written

$$\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2 = \frac{(\delta v)^2}{16\pi V_A(\Delta r)^4} \times\iiint_{r_0}^{\infty}\left(\frac{r\cos\theta}{r'^3} - \frac{\Delta r^2}{r'^3} - \frac{r\cos\theta}{r^3}\right)^2 \times r^2\sin\theta\, dr\, d\theta\, d\phi\ . \tag{A6}$$

Since $r'^2 = r^2 - 2r\,\Delta r\cos\theta + \Delta r^2$, we integrate (A6), obtaining as $\Delta\vec{r}\to 0$

$$\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2 = \frac{4}{45}\,\frac{(\delta v)^2}{V_A V_0}\ , \tag{A7}$$

where V_0 is the excluded volume $(\frac{4}{3}\pi r_0^3)$.

Before proceeding, we need an appropriate value for V_0. It can certainly be no smaller than the volume of an octahedral hole in the fcc lattice and is thus greater than $\frac{1}{20}V_A$.

For hydrogen in nickel,[25] $\delta v / V_A \simeq 0.3$, and we have the result

$$\sum_{i\neq 1}^{N}\left(\frac{d_{ip}}{d_{1p}}\right)^2 \leq \frac{1}{6}\ . \tag{A8}$$

APPENDIX B

Consider the reactions

$$\tfrac{1}{2}\mathrm{H}_2 + n\,\mathrm{Ni} = \mathrm{HNi}_n\ , \tag{B1a}$$

$$\tfrac{1}{2}\mathrm{D}_2 + m\,\mathrm{Ni} = \mathrm{DNi}_m\ , \tag{B1b}$$

$$\tfrac{1}{2}\mathrm{T}_2 + p\,\mathrm{Ni} = \mathrm{TNi}_p\ , \tag{B1c}$$

where these equations represent the reaction of hydrogen with Ni to form a dilute solid solution. We may write at equilibrium

$$\mu_\mathrm{H} = \tfrac{1}{2} G_{\mathrm{H}_2}\ , \tag{B2a}$$

$$\mu_\mathrm{D} = \tfrac{1}{2} G_{\mathrm{D}_2}\ , \tag{B2b}$$

$$\mu_\mathrm{T} = \tfrac{1}{2} G_{\mathrm{T}_2}\ , \tag{B2c}$$

where the μ_i are the chemical potential, or, in another nomenclature, the partial molar free energy of the dissolved hydrogen and G_i are the free energies of the corresponding gas. We now write the appropriate expressions for both the solid and gas phases and, making use of the foregoing equalities, obtain (assuming ideal solutions)

$$\mu_\mathrm{H} = \mu_\mathrm{H}^0 + RT\ln[\mathrm{H}] = \tfrac{1}{2}(G_{\mathrm{H}_2}^0 + RT\ln P_{\mathrm{H}_2})\ , \tag{B3a}$$

$$\mu_\mathrm{D} = \mu_\mathrm{D}^0 + RT\ln[\mathrm{D}] = \tfrac{1}{2}(G_{\mathrm{D}_2}^0 + RT\ln P_{\mathrm{D}_2})\ , \tag{B3b}$$

$$\mu_\mathrm{T} = \mu_\mathrm{T}^0 + RT\ln[\mathrm{T}] = \tfrac{1}{2}(G_{\mathrm{T}_2}^0 + RT\ln P_{\mathrm{T}_2})\ . \tag{B3c}$$

Under standard conditions,

$$P_{\mathrm{H}_2} = P_{\mathrm{D}_2} = P_{\mathrm{T}_2} = 1\ .$$

We can now subtract Eqs. (B3), pairwise, to obtain, for example,

$$\mu_\mathrm{H}^0 - \mu_\mathrm{D}^0 + RT\ln[\mathrm{H}]/[\mathrm{D}] = \tfrac{1}{2}(G_{\mathrm{H}_2}^0 - G_{\mathrm{D}_2}^0)\ . \tag{B4}$$

We must now select a standard state for the hydrogen and characterize the state corresponding to μ_H^0, μ_D^0, and μ_T^0. The latter are conveniently taken as the chemical potential of hydrogen dissolved in Ni at infinite dilution. By subtracting μ_D^0 from μ_H^0, we are left with only that portion of the free energy which depends solely upon the mass, i.e., the chemical effects to a first approximation cancel. If we take as the standard state the individual gaseous atoms H, D, and T at rest, we have thus chosen $G_\mathrm{H} = G_\mathrm{D} = G_\mathrm{T}$ in the standard state. Hence,

$$\mu_\mathrm{H}^0 - \mu_\mathrm{D}^0 = RT\ln\left(\prod_{j=1}^{3N+3} \frac{e^{-h\nu_j^\mathrm{H}/kT}}{1-e^{-h\nu_j^\mathrm{H}/kT}} \Bigg/ \prod_{j=1}^{3N+3} \frac{e^{-h\nu_j^\mathrm{D}/2kT}}{1-e^{-h\nu_j^\mathrm{D}/kT}}\right). \tag{B5}$$

If we now assume that the hydrogen is completely decoupled from the host crystal, we can rewrite Eq. (B5)

$$\mu_\mathrm{H}^0 - \mu_\mathrm{D}^0 = -RT\sum_{i=1}^{3}\ln\left[\frac{\sinh(h\nu_i^\mathrm{D}/2kT)}{\sinh(h\nu_i^\mathrm{H}/2kT)}\right]\ . \tag{B6}$$

Now, assuming a completely symmetric parabolic potential energy well for the hydrogen, we can write

$$\mu_\mathrm{H}^0 - \mu_\mathrm{D}^0 = -3RT\ln\left[\frac{\sinh(h\nu/\sqrt{2}\,kT)}{\sinh(h\nu/kT)}\right]\ . \tag{B7}$$

Following EKO[3] this may be conveniently written

$$\frac{\mu_\mathrm{H}^0 - \mu_\mathrm{D}^0}{RT} = -3\ln\left[\frac{f(\theta/\sqrt{2}\,T)}{f(\theta/T)}\right] + \tfrac{3}{2}\ln 2\ , \tag{B8}$$

where

$$f\left(\frac{\theta}{T}\right) = \frac{2\sinh(\theta/2T)}{\theta/T}$$

and $\theta = h\nu/k$. Substituting into Eq. (B4) and explicitly taking account of the standard state, we finally obtain for the ratio of the solubilities

$$\ln\frac{[\mathrm{H}]}{[\mathrm{D}]} = 3\ln\frac{f(\theta/\sqrt{2}\,T)}{f(\theta/T)} - \tfrac{3}{2}\ln 2 + \frac{1}{2}\,\frac{\Delta G_{\mathrm{H}_2}^0 - \Delta G_{\mathrm{D}_2}^0}{RT}\ . \tag{B9}$$

See Ref. 26 for the values for the last term on the right-hand side of (B9).

APPENDIX C

The partition function for an anharmonic linear oscillator is

$$q_A = \textstyle\sum_n e^{-E_n/kT}\ , \tag{C1}$$

where E_n is given by Eq. (22). This can be written as

$$q_A = e^{-u/2}\, e^{-ux/2} \textstyle\sum_n e^{-nu}\, e^{-n(n+1)ux}\ , \tag{C2}$$

where, as before, $u = h\nu/kT$ and $x = \phi/\theta$. By expanding the second exponential and ignoring terms of order x^2, we have

$$q_A = e^{-u/2}\, e^{-ux/2} \textstyle\sum_n e^{-nu}(1 - n^2 ux - nux)\ . \tag{C3}$$

Since $\sum_n e^{-nu} = (1-e^{-u})^{-1}$, the sums involving powers of n can be evaluated by noting that

$$\begin{aligned} -\frac{d}{du}\left(\sum_n e^{-nu}\right) &= \sum_n n\, e^{-nu}\ , \\ \frac{d^2}{du^2}\left(\sum_n e^{-nu}\right) &= \sum_n n^2 e^{-nu}\ . \end{aligned} \tag{C4}$$

Making use of (C4), we can write

$$q_A = e^{-u/2}(1-e^{-u})^{-1}[1 - 2xu\, e^{-u}(1-e^{-u})^{-2}]\, e^{-ux/2}\ . \tag{C5}$$

We note that this differs from the usual expression[27] for an anharmonic oscillator, since we have expressed q in terms of the frequency of the unperturbed harmonic oscillator instead of that associated with the first-level spacing of the anharmonic oscillator.

The partition function for a harmonic oscillator is

$$q = e^{-u/2}(1 - e^{-u})^{-1} \equiv (2\sinh\tfrac{1}{2}u)^{-1} . \qquad \text{(C6)}$$

Since the function $f^{-1} = uq$, we can rewrite Eq. (C5) as

$$\frac{1}{f_A} = \frac{1}{f}\left(1 - \frac{2x}{u}\frac{1}{f^2}\right)e^{-ux/2} . \qquad \text{(C7)}$$

The cube of this expression is appropriate for hydrogen in the equilibrium configuration, since the dominant anharmonic correction was $\sim(\Delta x^4 + \Delta y^4 + \Delta z^4)$, thus allowing the three equilibrium modes to be treated independently.

In the saddle point, however, the dominant anharmonic term becomes $\sim(\Delta x^2 + \Delta y^2)^2$ rather than $\sim(\Delta x^4 + \Delta y^4)$. Thus we need to evaluate the partition function for an anharmonic two-dimensional oscillator given by

$$q'_A = \sum_{n,m} e^{-E_{n,m}/kT} , \qquad \text{(C8)}$$

where $E_{n,m}$ is given by Eq. (28). Thus,

$$q'_A = e^{-u'} e^{-4/3u'x'} \sum_m \sum_n e^{-nu'} e^{-n(n+2)u'x'} e^{+1/3mu'x'} . \qquad \text{(C9)}$$

Expanding the last exponential, we have

$$\sum_m e^{1/3mux} = \sum_m (1 + \tfrac{1}{3}m^2u'x')$$

$$= (n+1)[1 + \tfrac{1}{9}n(n+2)u'x'] , \qquad \text{(C10)}$$

since $m = \pm(n,\ n-2,\ n-4,\ \ldots,\ 0 \text{ or } 1)$. The sum was evaluated as a second-order arithmetic progression. Proceeding as before, we obtain

$$q'_A = e^{-u'}(1 - e^{-u'})^{-2}[1 - 4ux\, e^{-u'}(1 - e^{-u'})^{-2}]\, e^{-4u'x'/3} , \qquad \text{(C11)}$$

or, in terms of f',

$$\frac{1}{f_A'^2} = \frac{1}{f'^2}\left(1 - 4\frac{x}{u}\frac{1}{f'^2}\right)e^{-4u'x'/3} . \qquad \text{(C12)}$$

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*Present address: Bell Telephone Laboratories, Allentown, Pa. 18103.

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