transitions in solids. The techniques are also applicable to partially absorbed light which will be modulated by transverse magnetization in the ground state. The procedure is reversible in this case in that circularly polarized light modulated at the Larmor frequency (or pulsed rapidly in comparison with the Larmor period) can induce transverse magnetization into both the ground and excited states. Both of these techniques have been applied in atomic spectroscopy[10],[11] and modulation experiments have been proposed[12] utilizing the R lines of ruby as well as other paramagnetic systems. The recent development of rapidly pulsed and modulated laser outputs may lead to many interesting optical pumping experiments along these lines.

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RELAXATION PROCESS DUE TO LONG-RANGE DIFFUSION OF HYDROGEN AND DEUTERIUM IN NIOBIUM

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We have applied a new method for the determination of diffusion coefficients to hydrogen and deuterium in niobium. The activation energies for both isotopes are comparatively small and differ by about 20%, whereas D_0 is the same within experimental error. The activation energy for hydrogen diffusion is equal to the energy difference $\hbar\omega_H = 114 \pm 6$ meV between the ground state and the first excited state of the hydrogen atom in solution.

Mobile point defects with strain fields of lower symmetry than the lattice give rise to a relaxation process of the Snoek type. Yet any point defect—asymmetric or symmetric—will be the source of another type of relaxation process, if the point defects cause lattice parameter changes and the applied stress produces a gradient in lattice dilatation. The point defects will follow the gradient of dilatation similar to the phonons in the thermoelectric damping process.[1] This relaxation process due to long-range diffusion of point defects was proposed by Gorsky[2] in 1935. The experimental verification of this process has suffered from the extremely long time required generally for particle diffusion over distances of

specimen dimensions (e.g., 1 yr for oxygen in a 1-mm-diam niobium specimen at 300°C).

We have found that the Gorsky effect is conveniently measurable for hydrogen and deuterium in niobium and thus offers a new method with widespread applicability for determining diffusion coefficients for solid systems with high diffusivity. The diffusion coefficients for hydrogen and its isotopes are difficult to measure. Using permeation methods, the main experimental problem is the slowness of the surface reaction when compared with the rate of bulk diffusion. The Gorsky-effect method is free from the problem of permeation through external surfaces.

Niobium wire was outgassed at 2200°C and

10^{-10} Torr for several hours. The wire was wound into a coiled spring, recrystallized to give a grain size of the order of the wire diameter, and loaded with 1.2-at.% hydrogen at 500°C. Elastic aftereffect measurements were performed in an inverted pendulum.

The relaxation process turned out to be a simple exponential function with a relaxation strength of 1.6% per 1-at.% hydrogen and a relaxation time of 160 sec at room temperature for a specimen with 1.25 mm diam.

For cylindrical specimens with the diameter d, the relaxation time τ is related to the diffusion coefficient D by[1]

$$13.55 D\tau = d^2. \tag{1}$$

Measurements on two samples with different diameters (1.25 and 0.76 mm) did indeed show the d^2 dependence of the relaxation time at given temperatures. For both series of measurements the diffusion coefficient was calculated using Eq. (1) and plotted in Fig. 1. In the temperature range of 270 to 560°K the diffusion coefficient of hydrogen obeys an Arrhenius relation with an activation energy of 110 ± 5 meV and $D_0 = (5.4 \pm 0.6) \times 10^{-4}$ cm^2/sec. This activation energy is about a factor of 10 smaller than that reported for example for oxygen in Nb[3] and is also appreciably lower than the 180 meV found by Cannelli and Verdini[4] for an internal friction process in hydrogen-loaded niobium at 100°K and 30.7 kHz.

The "attempt frequency" ν can be determined assuming either octahedral-octahedral ($D_0 = a^2\nu/24$) or tetrahedral-tetrahedral ($D_0 = a^2\nu/64$) jumps with the following result ($a = 3.30$ Å):

$$\nu_{o-o} = (1.2 \pm 0.1) \times 10^{13} \text{ Hz},$$

$$\nu_{t-t} = (3.2 \pm 0.3) \times 10^{13} \text{ Hz}.$$

These frequencies are about a factor 40 smaller than the corresponding values for oxygen interstitials in Nb[3] but still higher than 6×10^{12} Hz, which is the highest phonon frequency of the unloaded Nb lattice.[5]

A diffusion coefficient for hydrogen at 200°C, as determined by quasielastic neutron scattering,[6] is included in Fig. 1 and happens to fall on the deuterium line. The neutron-scattering value differs by about a factor of 2 from our value. A subsequent series of measurements on the 1.25-mm specimen loaded with 2.5 at.% deuterium gives the following results: The activation energy increased to 135 ± 5 meV, whereas $D_0 = (5.6$
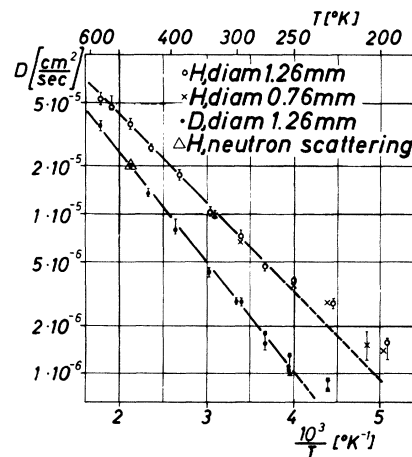

FIG. 1. Diffusion coefficient of hydrogen and deuterium in niobium.

$\pm 0.6) \times 10^{-4}$ cm^2/sec was found to be the same as the previously determined value for hydrogen. Also within experimental error, the relaxation strength did not differ from that of hydrogen.

From inelastic neutron scattering[6] two energy levels for the hydrogen atom in niobium have been found at 114 ± 6 meV and $177 \pm$ meV. It is interesting to note that one energy level is appreciably higher than the energy barrier for diffusion, whereas the lower energy level (which for the octahedral position corresponds to the oscillation towards the saddle point) coincides within the experimental errors with the activation energy for diffusion.

From a rate-theory approach to diffusion[7] these results can be interpreted as follows: The difference $\Delta U = 25 \pm 10$ meV in activation energy is attributed to the lower zero-point energy of deuterium.[7-9] If in a first-order approximation the same lattice potential for both isotopes is assumed, the zero-point energies for the modes of oscillation towards the saddle point differ by $\Delta U = \frac{1}{2}\hbar\omega_H[1 - (m_H/m_D)^{1/2}]$, which is 17 meV with $\hbar\omega_H = 114$ meV.[6] The absence of an isotope dependence for D_0 has been predicted by Ebisuzaki, Kass, and O'Keeffe[9] in a semiclassical extension of rate theory for low temperatures ($T \ll \hbar\omega_H/k = 1370$°K) and indicates that D_0 is determined by the motion of the host lattice only. The coincidence of the hydrogen activation energy with the energy difference for two states of the hydrogen atom in solution is in this picture purely accidental, but consistent with the concept that the saddle point exists only statistically.

On the other hand this coincidence could be in-

terpreted as indicating a band-type proton motion in niobium.[10] In this picture of a nondegenerate proton semiconductor the temperature dependence of the diffusion constant is given by that of the proton concentration in the conduction band. The stronger temperature dependence for deuterium can be attributed to a larger bandgap. However, it is also possible that for deuterium, compared with hydrogen, the next higher band gives the main contribution to deuteron conduction. A discussion of the isotope dependence of D_0 in the band model requires a more detailed knowledge of the band properties. A realistic theoretical band model for the proton mobility will have to take into account the local lattice distortion caused by the proton when located in interstitial sites. Therefore, a model similar to the polaron appears to have a good chance for a successful description of the results.

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LOW-TEMPERATURE THERMOPOWER OF DILUTE ALLOYS*

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A new mechanism—the virtual recoil of solute ions—is investigated and shown to cause the dominant contribution to the thermopower of dilute alloys at low temperatures.

The fact that the magnitude and sign of the thermopower of dilute alloys is a strong function of the specific type of solute present has been well established,[1-6] and has long been an unsolved theoretical problem. In this Letter, it is shown that a major contribution to the low-temperature thermopower arises from the virtual recoil of the solute ions. Using a free-electron model we indicate how by taking this mechanism into account qualitative agreement between theory and experiment can be obtained for alloys of alkali metals in K.

The electron-diffusion thermopower S is given to first order in temperature T by the well-known relationship[7]

$$S = (\pi^2 k^2 T/3e)[\partial \ln\sigma(\epsilon)/\partial\epsilon]_{\epsilon=\zeta}, \qquad (1)$$

where $\sigma(\epsilon)$ is the conductivity which the sample would have at $T=0$ if the Fermi energy were ϵ and is given by

$$\sigma(\epsilon) = -(e^2/\Omega)D(\epsilon)v^2(\epsilon)\tau(\epsilon). \qquad (2)$$

Here Ω is the volume of the sample, $D(\epsilon)$ the energy density of electron states, and $v(\epsilon)$ their group velocity. The relaxation time $\tau(\epsilon)$ is given by

$$1/\tau(\epsilon_{\vec{k}}) = \sum_{\vec{k}'} Q(\vec{k}, \vec{k}')(1-\cos\theta_{\vec{k}\vec{k}'}), \qquad (3)$$

with $Q(\vec{k}, \vec{k}')$, the probability per unit time that an electron is scattered from $\vec{k}$ to $\vec{k}'$, given by

$$Q(\vec{k}, \vec{k}') = (2\pi/\hbar)|T_{\vec{k}'\vec{k}}|^2 \delta(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'}), \qquad (4)$$

$T_{\vec{k}'\vec{k}}$ being the transition amplitude for scattering from k to k'. We determine $T_{\vec{k}'\vec{k}}$ taking as our model a gas of free electrons interacting with a random array of impurities through a potential $V(\vec{r}-\vec{l}-\vec{y}_{\vec{l}})$, $\vec{y}_{\vec{l}}$ being the displacement from equilibrium, due to lattice vibrations, of the impurity whose equilibrium position is $\vec{l}$. If for convenience we take $\vec{l}=0$, then in the notation of second quantization the operator V is given to first order in $\vec{y}$ by