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Diffusion of Hydrogen in Tantalum Studied by Motional Narrowing of Mössbauer Lines*

A. Heidemann, G. Kaindl,† D. Salomon,‡ H. Wipf, and G. Wortmann
Physik-Department der Technischen Universität München, D-8046 Garching, Germany

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The effects of H in Ta metal on the isomer shift and linewidth of the 6.2-keV Mössbauer resonance of ^{181}Ta have been studied as a function of H concentration and temperature. From the results, values for the activation energy of the H diffusion and for the mean residence time of the H atoms in Ta are derived.

The diffusional reduction of the linewidth (motional narrowing) is a well-established phenomenon in nuclear magnetic resonance and has been applied successfully in studies of diffusion.[1] Until now, similar motional-narrowing effects on Mössbauer resonance lines—though theoretically discussed[2] and observed in a limited case[3]—have not been utilized for obtaining quantitative information on the diffusion process. Using the high-resolution 6.2-keV γ resonance of ^{181}Ta,[4] we were able to observe the influence of the diffusion of H on the Mössbauer resonance in Ta metal. From the experimental results for the line shift and linewidth as functions of H concentration and temperature, the activation energy and the mean residence time of the diffusing H interstitial were derived. This opens a new microscopic method for studying the diffusion of H—and possibly other impurity atoms—in transition-metal hosts. The method is complementarily related to usual NMR studies of diffusion, since here the probes (the ^{181}Ta nuclei) are not diffusing by themselves, but are subjected to fluctuating interactions with the diffusing interstitials.

The experiments were performed on H-loaded Ta foils (4 mg/cm^2 thick; nominal purity 99.996 %), which were used as absorbers in Mössbauer transmission experiments with a single-line source of ^{181}W diffused into a single crystal of W metal. In order to ensure high purity, the Ta foils were degassed in ultrahigh vacuum ($\sim 10^{-9}$ Torr) and temperatures up to 2000°C. They were then electrolytically loaded with H in a $0.01N$ H_2SO_4 bath at current densities of about 100 mA/cm^2. The resulting H concentrations up to $c = 0.17$ (where c is defined as the H/Ta atom ratio) were obtained directly from the amount of H extracted at high temperatures from the loaded samples using a commercial vacuum-extraction apparatus.[5] According to the Ta-H phase diagram[6] and the experimental conditions, all samples studied were in the bcc α phase.

Some of the Mössbauer absorption spectra are presented in Fig. 1. The data were fitted with a single Lorentzian line modified by a constant dispersion term. This term describes the pronounced asymmetry of the lines and results solely from an interference between the Mössbauer ab-

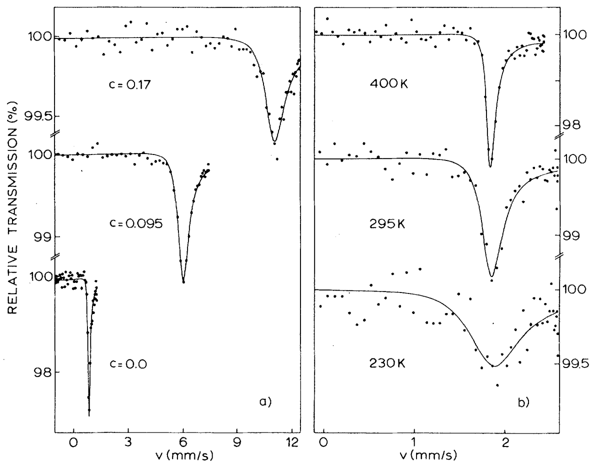

FIG. 1. ^{181}Ta Mössbauer absorption spectra of H-loaded Ta foils: (a) at room temperature (295 K) for various H concentrations c; (b) at $c = 0.018$ for different temperatures. The solid lines represent least-squares fits to the data with dipersion-modified Lorentzian lines, which are typical for the ^{181}Ta resonance (see text).

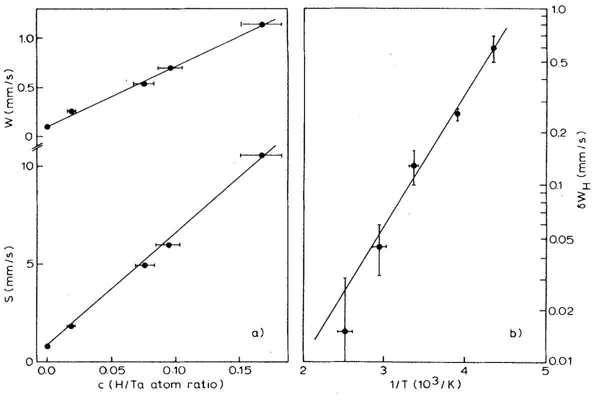

FIG. 2. (a) Plot of the fit results for the linewidth W and isomer shift S of the ^{181}Ta Mössbauer resonance at room temperature (295 K) as a function of H concentration c. (b) Semilogarithmic plot of the H-induced line broadening δW_H of the ^{181}Ta Mössbauer resonance versus reciprocal temperature for a Ta-H absorber with $c = 0.018$.

sorption followed by internal conversion and photoelectric absorption.[7] Two prominent effects are readily seen from Fig. 1(a): With increasing H concentration, the resonance line is strongly shifted to higher energies and broadens considerably. In addition, the H-induced line broadening exhibits a strong temperature dependence as can be seen from Fig. 1(b), while the H-induced lineshift does not change with temperature within the experimental accuracy. At $T = 400$ K the linewidth of the H-loaded absorber with $c = 0.018$ is almost identical to that of an unloaded one; the observed temperature dependence of the line broadening is reversible.

In Fig. 2(a) the fit results are summarized for the linewidth W and isomer shift S at room temperature. Within the studied concentration range, both quantities increase linearly with the concentration as $dS/dc = 57 \pm 6$ mm/sec and $dW/dc = 6.3 \pm 0.7$ mm/sec. dS/dc is independent of temperature, since the position of the resonance line of the absorber with $c = 0.018$ did not exhibit temperature shifts different from those of pure Ta metal.[8]

The concentration dependence of the isomer shift reflects changes in the electronic structure of Ta metal upon H loading and can be discussed in terms of existing models for the electronic structure of transition-metal–H systems.[9] Since the change in the mean square of the nuclear charge radius is negative for the 6.2-keV γ resonance, $\Delta\langle r^2\rangle \simeq -0.05$ fm^2,[4] the observed increase of S corresponds to a decrease in the total electron density $\rho(0)$ at the Ta nucleus with increasing c. As was concluded in Ref. 9, only part of the hydrogen electrons fill up d states of the Ta conduction band, causing the observed decrease of $\rho(0)$ with c. This is in agreement with the conclusions of a recent photoemission study of Pd-H.[10]

The following discussion will be devoted to the H-induced line broadening and its dependence on concentration and temperature. The line broadening results from fluctuations of the local H configuration around the Ta atom, modulating the γ-resonance energy either via changes of $\rho(0)$ at the Ta nucleus (isomer shift) or via electric-quadrupole interaction. The influence of such a modulation of the resonance energy on the Mössbauer spectrum can be described by the stochastic theory of Kubo,[11] which is also applicable to the case of γ resonance.[2]

For simplicity we make two assumptions: (i) Isomer-shift effects dominate electric-quadrupole effects in the H-induced modulation of the γ-resonance energy, and (ii) only H atoms in nearest-neighbor interstitial sites are assumed to influence the Ta isomer shift. The H atoms occupy tetrahedral interstitial sites in α-phase Ta-H[12]; there are six tetrahedral sites per Ta atom and 24 interstitial sites in nearest-neighbor positions to a Ta atom; therefore, the mean number of H atoms in all 24 nearest-neighbor sites is $4c$. Defining ω_H as the isomer shift caused by one H atom in a nearest-neighbor interstitial site, we can write the mean H-induced isomer shift S_H as

$$S_H = \omega_H \times 4c. \tag{1}$$

The linear dependence of S_H on c in Eq. (1) is in agreement with the experimental data [Fig. 2(a)]. From the observed concentration dependence of the isomer shift, ω_H is found to be 14.2 ± 1.5 mm/sec, corresponding to an angular frequency of $(4.5 \pm 0.5) \times 10^8$ sec^{-1}. In the following equations, all energy quantities (S_H, ω_H, etc.) will be given in angular frequencies.

If we describe the modulation of the resonance energy by the two parameters Δ and τ_c,[11] where Δ is the amplitude of the modulation and τ_c is the correlation time, the limit of fast modulation (motional-narrowing limit) is given by the condition $\Delta\tau_c \ll 1$. It will be shown later that this condition is well fulfilled in the present work. In this case, the resonance line has Lorentzian shape,[2,11] which is modified for the ^{181}Ta resonance by the dispersion term.[7] The H-induced increase of the linewidth (full width at half-maximum) δW_H, which is not affected by the dispersion term,[7] is given by[2,11]

$$\delta W_H = 2 \times \Delta^2 \tau_c. \tag{2}$$

For the low H concentrations studied in the present work, Δ^2 can be written as

$$\Delta^2 = \omega_H^2 \times 4c, \tag{3}$$

where Δ^2 is the mean square deviation of the isomer shift from its mean value S_H. In Eq. (3), $4c$ stands for the mean square deviation of the total number of H atoms occupying the 24 nearest-neighbor tetrahedral sites of a Ta atom from the mean value $4c$ (for low H concentrations, the mean square deviation is equal to the mean value). The correlation time τ_c is proportional to the mean residence time τ_r of the H atoms on interstitial sites, $\tau_c = n\tau_r$. It can be shown that n is equal to the average number of times that a single H atom, starting from a nearest-neighbor interstitial site of a Ta atom, will occupy any one of the 24 nearest-neighbor interstitial sites of the same Ta atom in the course of its diffusion.[13] We have calculated this number as $n = 12.6 \pm 0.5$ with a Monte Carlo method, assuming uncorrelated jumps between next-nearest interstitial sites.

From the above equations the line broadening can be written as

$$\delta W_H = 8cn\omega_H^2 \tau. \tag{4}$$

Using Eqs. (1), (3), and (4), the condition for the limit of fast modulation, $\Delta\tau_c \ll 1$, can be rewritten as

$$(\delta W_H / S_H)\sqrt{c} \ll 1, \tag{5}$$

which is well fulfilled in the present case.

The linear dependence of δW_H on c in Eq. (4) is in agreement with the experimental results [Fig. 2(a)]. With Eq. (4) and $n = 12.6$ a value of $\tau_r = (9.8 \pm 1.5) \times 10^{-12}$ sec at room temperature (295 K) can be derived from the concentration dependence of the linewidth. The observed temperature dependence of the line broadening is contained in the proportionality of δW_H to τ_r in Eq. (4). With $\tau_r \propto \exp(U/kT)$, where U is the activation energy of the diffusion process, a temperature dependence of $\delta W_H \propto \exp(U/kT)$ is expected. According to Fig. 2(b), such a temperature dependence is observed resulting in $U = 0.14 \pm 0.01$ eV. The results for τ_r and U are in good agreement with those derived from macroscopic diffusion measurements.[6] Particularly, the result for τ_r strongly supports the validity of the assumptions made in our model, where the effects of electric-quadrupole interaction and of further-distant H interstitials on the resonance line have been neglected. In addition, recent nuclear-acoustic-resonance measurements[14,15] on Ta-H show that electric quadrupole contributions to the H-induced line broadening of the Mössbauer resonance line are about ten times smaller than the effects of isomer-shift fluctuations. It should be added, however, that the result for U is not expected to depend on these assumptions.

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†Present address: Abteilung für Physik und Astronomie, Ruhr-Universität Bochum, D-463 Bochum, Germany.

‡Present address: Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1 Berlin 33, Germany.

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Nonlinear Excitation of Surface Polaritons

F. De Martini* and Y. R. Shen
Department of Physics, University of California, Berkeley, California 94720, and
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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We show that nonlinear excitation of surface-polariton waves by optical mixing should be possible. The excited surface waves can be easily detected by either the prism-coupling method or coherent scattering from wave mixing. Practical numerical examples are given.

Surface physics has recently attracted a great deal of attention. Accordingly, there has also been increasing interest in the problem of surface polaritons. The methods of investigation of surface polaritons are however limited. So far, surface polaritons and plasmons have been studied by inelastic electron diffraction,[1] by attenuated total optical reflection,[2] and by Raman scattering.[3,4] Optical second-harmonic generation has also been used to probe the coupling between the fundamental field and the surface plasmons.[5] One would expect that surface polaritons can also be nonlinearly excited by optical mixing of two laser beams. In this Letter, we show that this is indeed possible with ordinary pulsed dye lasers. We present for the first time a formulated theory of nonlinear excitation of surface polaritons. This theory can be easily extended to other problems involving nonlinear coupling of surface polaritons with bulk electromagnetic waves. We propose to detect the excited surface polaritons by either the prism method in which the surface waves are coupled out by a prism or the wave-mixing scheme in which the surface waves coherently scatter a probe beam.

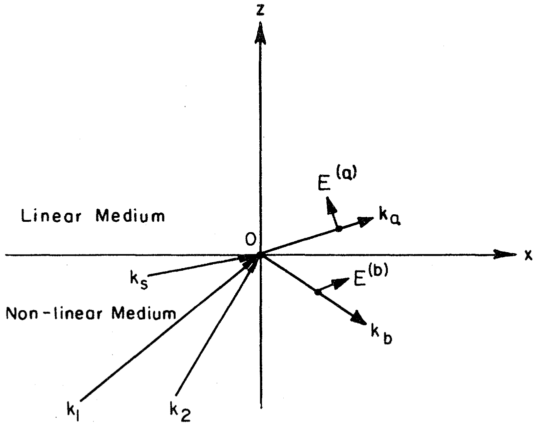

FIG. 1. Difference-frequency generation at a boundary surface. The wave vectors of incoming pump waves, the nonlinear polarization wave, and the difference-frequency waves are shown.