Nuclear-acoustic-resonance studies of the Ta-H system: An interpretation that characterizes the hydride precipitate

R. K. Sundfors
Laboratory for Ultrasonics, Physics Department, Washington University, St. Louis, Missouri 63130

T. H. Wang
Physics Department, Southern University and A&M College, Baton Rouge, Louisiana 70813

D. G. Westlake
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 1 August 1983)

Previously measured nuclear-acoustic-resonance linewidths at low concentrations of hydrogen in tantalum metal at 78 K show a very strong linewidth anisotropy as an external magnetic field is varied. This anisotropy produces the greatest linewidth in ⟨100⟩ directions and the anisotropic part of the linewidth increases with hydrogen concentration. At 78 K almost all of the hydrogen is present as a precipitate of tantalum hydride in the tantalum lattice. It is shown that the measured linewidths can be explained by an isotropic contribution and an anisotropic contribution due to electric field gradients in ⟨100⟩ directions in different parts of the single crystal and that the anisotropic contribution increases with increasing hydrogen concentration. It is concluded that the elastic strain due to the hydrogen precipitate must exist in ⟨100⟩ directions, and this is shown to be consistent with previous optical metallography and transmission-electron-microscopy measurements.

I. INTRODUCTION

Dynamic quadrupole coupling[1] has been used in many nuclear acoustic resonance (NAR) investigations[2–13] of ^{181}Ta in single-crystal tantalum with low concentrations of hydrogen impurities. Because of the large quadrupole moment (3.9 b) and large Sternheimer antishielding factor (estimated[3] to be 220) and the fact that NAR line shapes do not have contributions from the $-\frac{1}{2}$ to $\frac{1}{2}$ transition, the observed NAR line shapes and linewidths are strongly affected by electric field gradients due to ionized impurities and lattice strain. In particular, NAR measurements of the linewidths of ^{181}Ta can give detailed information about the hydrogen atoms which have precipitated as β-hydride particles dispersed in the α matrix at 78 K. Optical metallography measurements[14] of these precipitates at the surfaces of single crystals reveal that they have {100} habit planes. Transmission electron microscopy measurements[15] of the β-phase (Ta_2H) particles at hydrogen concentrations exceeding 10 at.% reveal that the largest lattice expansion is along a ⟨100⟩ direction. Earlier, the anisotropy of the $\Delta m = \pm 2$ NAR linewidth for Ta crystals containing less than 2 at.% hydrogen was measured[3] as the angle between the external magnetic field and the [001] direction was varied. The present interpretation of those experiments is consistent with the description given above for the β-hydride precipitates dispersed in the α matrix.

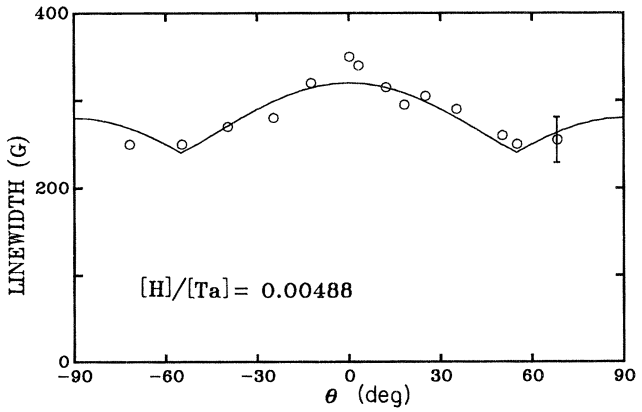

FIG. 1. $TaH_{0.00488}$ NAR linewidth vs magnet angle for magnet-angle variation in a (110) plane. The sample was cooled slowly over 6 h from 300 to 78 K. Open circles are the experimental points and the solid line is the computed fit. $\theta = 0°$ is a [001] direction.

II. RESULTS

A. Linewidth analysis

The NAR $\Delta m = \pm 2$ line shape in the $\alpha+\beta$ alloy consists of a broad resonance and an apparent narrow resonance. The narrow resonance is believed to be an anomaly[13] explained by Fedders's theory[16,17] of intra-spin isocross relaxation. Ströbel *et al.*[2] have measured an isotropic broad resonance in $TaH_{0.0014}$ and in $TaH_{0.0029}$ at 78 K. At the same temperature, Wang[3] measured the linewidth dependence of the broad line on angle for $TaH_{0.00488}$ (Fig. 1), for $TaH_{0.0115}$ (Fig. 2), and for

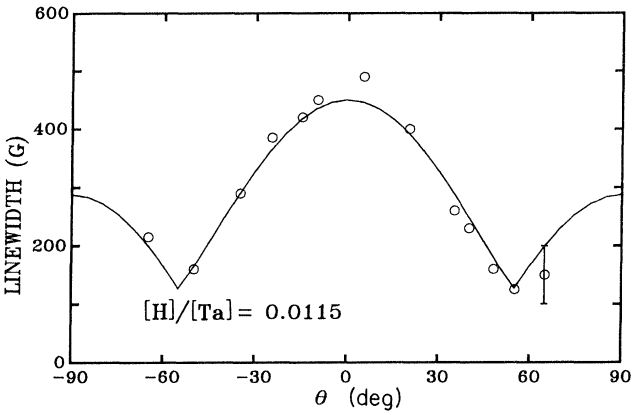

FIG. 2. $TaH_{0.0115}$ NAR linewidth vs magnet angle for magnet-angle variation in a (110) plane. The sample was cooled slowly over 6 h from 300 to 78 K. Open circles are the experimental points and the solid line is the computed fit. $\theta = 0°$ is a [001] direction.

$TaH_{0.0116}$ (Fig. 3). In Figs. 1—3, the magnetic field was rotated in a (110) plane. The tantalum single crystals of Figs. 1 and 2 were cooled from 300 to 78 K over a period of 6 h while the tantalum single crystal of Fig. 3 was cooled through the same temperature range in 30 min. The samples of Figs. 2 and 3 were studied at 78 K with no previous cool down through the solvus temperature since the samples were annealed and charged with hydrogen. The sample of Fig. 1 was cooled and warmed through the solvus temperature several times before the data of Fig. 1 were taken.

The above data on the broad linewidth variation with magnet angle at different hydrogen concentrations indicate that there is an isotropic contribution to the broad linewidth which dominates at the lowest hydrogen concentrations and an anisotropic contribution which can first be seen for hydrogen concentrations between $TaH_{0.0029}$ and $TaH_{0.00448}$. The anisotropic contribution increases as the hydrogen concentration increases and is

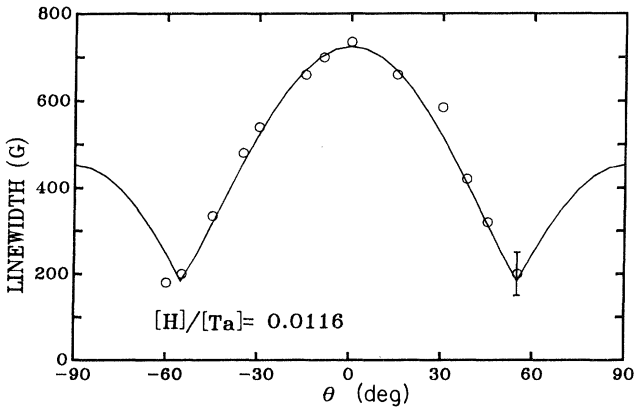

FIG. 3. $TaH_{0.0116}$ NAR linewidth vs magnet angle for magnet-angle variation in a (110) plane. This sample was cooled quickly (in less than 30 min) from 300 to 78 K. Open circles are the experimental points and the solid line is the computed fit. $\theta = 0°$ is a [001] direction.

maximum in the [001] direction, when the magnetic field is rotated in a (110) plane. During the magnetic field rotation, there is a single broad resonance line shape which varies in width.

The anisotropic linewidth variation can be explained if there are electric field gradients (EFG) along the [100], [010], and [001] directions in different parts of the single crystal which affect the tantalum atoms. Independent of which ⟨100⟩ direction the EFG is taken, the electric-field-gradient component V_{zz} computed along the direction of the external magnetic field as it rotates in a (110) plane has the same angular dependence $(3\cos^2\theta - 1)$, where θ is the angle between the magnetic field direction and the [001]. In order to analyze the data in Figs. 1—3, we write

$$\Delta = K(3\cos^2\theta - 1)/2 \ , \qquad (1)$$

where K is the difference in Δ between $\theta = 0°$ and 54.75°. If the total linewidth is the sum of isotropic and anisotropic contributions, then at $\theta = 54.75°$ the anisotropic contribution should be zero and the measured width is the isotropic contribution. It should be noted that the isotropic contribution in the sample of Fig. 1, which was cycled through the solvus temperature several times, is larger than the samples of Figs. 2 and 3, which were studied in their first cool down through the solvus temperature. The linewidth in the two samples of lower hydrogen concentrations studied by Ströbel *et al.*[2] increased with hydrogen concentration. As suggested by Ströbel *et al.*, it is possible that the isotropic linewidth is caused by an increase in the number of local dislocations associated with the hydride precipitate particles after thermal cycling of samples through the solvus temperature. We therefore expect that the isotropic linewidth will increase with the number of hydrogen impurities and also be dependent on the thermal history of the sample.

The lines drawn through the data points in Figs. 1—3 have been determined as follows. We first assume that the ^{181}Ta line shape does not change as the linewidth broadens. Then the anisotropic linewidth should be proportional to the electric field gradient causing the broadening at any given angle. The isotropic contribution is found from the linewidth at $\theta = 54.75°$ and is subtracted from the linewidth at $\theta = 0°$, which gives the amplitude of the anisotropic contribution. Anisotropic linewidth contributions from Eq. (1) are then computed and added to the isotropic linewidths which give the computed linewidths and are plotted as the solid lines in Figs. 1—3.

We note that the good agreement in Figs. 1—3 indicates that the linewidth anisotropy is explained by EFG in different ⟨100⟩ directions at ^{181}Ta nuclear positions at different positions in the single crystal. Since the magnitude of the anisotropic contribution increases with hydrogen concentration, the anisotropic broadening is probably caused by hydride precipitation producing strain in different ⟨100⟩ in different parts of the single crystal, which thereby destroys the cubic symmetry at the tantalum nuclear position. This conclusion is consistent with the determination that the Ta_2H platelets have {100} habit planes[14] and that the largest expansion in the platelets is

in ⟨100⟩ directions.[15]

As noted above, a *single* broad resonance line shape was measured as the magnetic field was rotated in the (110) plane. A single resonance line shape in this case suggests one type of tantalum nuclear position, namely that in which there is a ⟨100⟩ EFG. We note that the strain contribution to the EFG is known to fall off[18] as r^{-3}, where r is the distance from the source of the strain to the position where the EFG is measured. One explanation of the single line shape is that ⟨100⟩ direction strain fields extend many lattice constants beyond the strain sources, so that most tantalum nuclear positions "see" one of the possible ⟨100⟩ strains depending on position in the tantalum single crystal.

B. Elastic strain estimate

By comparing the data for Figs. 2 and 3, we see a large increase in the anisotropic line broadening for an insignificantly small change in hydrogen concentration. We conclude that the faster rate of cooling for the sample in Fig. 3 caused additional strain in ⟨100⟩ directions possibly because fewer prismatic dislocation loops were punched out by the precipitating platelets and larger residual coherency stresses resulted.

An estimate of the average strain at those tantalum atoms which experience anisotropic linewidth broadening can be made. We take the measured anisotropic line broadening of 340 G for $TaH_{0.0115}$ (Fig. 2) and define its square as the second moment. The second moment due to quadrupole broadening has been determined by Bersohn[19] for nuclear magnetic resonance line shapes and extended to NAR line shapes.[20] The second-moment contribution for $\Delta m = \pm 2$ transitions can be written[20] as

$$\langle \hbar^2(\Delta\omega)^2\rangle_{\rm av} = (144/7)[I(I+1)-2]N^{-1}\sum_{j=0}^{\infty} E_j^2 \ , \quad (2)$$

where

$$E_j = eQ[4I(2I-1)]^{-1}\left[\frac{\partial^2 V}{\partial z^2}\right]_j = A(V_{zz})_j$$

and

$$V_{zz} = (S_{11}-S_{12})\epsilon_{zz} \ .$$

In the above equations, I is the nuclear spin, N is the number of nuclear spins/cm^3 which contribute to the second moment, Q is the electric quadrupole moment of the nucleus, and S_{11} and S_{12} are components of the tensor relating the electric field gradient V_{zz} to the elastic strain component ϵ_{zz}. From Eq. (2), the square root of the average square strain at a tantalum nuclear position that experiences the anisotropic broadening can be estimated as 3×10^{-4}, where the following values are used: $I=\frac{7}{2}$, $Q = 3.9$ b, $S_{11}-S_{12} = 28\times10^{15}$ statvolt cm^{-2}.[21,22] Such large strains in the vicinity of hydride platelets are probably not surprising; Asano *et al.*[23] have shown that converting α-Ta to β-Ta_2H causes the cubic Ta lattice with $a_0 = 3.3027$ Å (Ref. 24) to distort to a monoclinic sublattice of Ta atoms with $a = b = 3.359$ Å, $c = 3.398$ Å, and $\gamma = 90.3°$. Thus the c axis expands by about 2.89% while a and b are expanding about 1.70%. Obviously, there is a large discrepancy between this anisotropic strain generated by the formation of the β-phase platelet and the average strain of approximately 3×10^{-4} that was calculated above for those nuclei that are responsible for the anisotropic contribution to the linewidth. This discrepancy is consistent with the idea that the anisotropic strain generated at the platelet is distributed elastically in the α phase over a distance that is many times greater than the thickness of the β-phase platelet. Thus, even though the β phase constitutes only a small fraction of the sample volume, a large fraction of the Ta nuclei in the sample contributes to the anisotropic part of the measured linewidth.

III. SUMMARY

The analysis of the large linewidth anisotropy of ^{181}Ta NAR, which increases with hydrogen concentration, shows that it can be explained by elastic strain in ⟨100⟩ directions from Ta_2H precipitates, which have their largest expansions in ⟨100⟩ directions. The magnitude of the average strain seen by the ^{181}Ta spin system is estimated from the linewidth broadening to be 3×10^{-4}. The fact that a single resonance line shape was observed as the magnetic field was rotated in the (110) plane is suggested as evidence that oriented strain extends many lattice constants beyond the source of the strain.

ACKNOWLEDGMENTS

This research was carried out with financial assistance of the National Science Foundation under Grant No. DMR-81-06142 and with the support of the United States Department of Energy.

[1]D. I. Bolef, *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1966), Vol. IVA.
[2]B. Ströbel, K. Läuger, and H. E. Bömmel, Appl. Phys. 9, 39 (1976).
[3]T. H. Wang, Ph.D. thesis, Washington University, 1974.
[4]B. Ströbel, K. Läuger, D. Schilling, and H. E. Bömmel, Phys. Rev. Lett. 26, 2114 (1980).
[5]D. Schilling, K. Läuger, B. Ströbel, and H. E. Bömmel, Phys. Status Solidi B 105, K129 (1981).
[6]R. E. Smith and D. I. Bolef, Phys. Rev. Lett. 22, 183 (1969).
[7]R. E. Smith, Ph.D. thesis, Washington University, 1969.
[8]R. G. Leisure, D. K. Hsu, and B. A. Seiber, Phys. Lett. 42A, 3394 (1973).
[9]R. G. Leisure, D. K. Hsu, and B. A. Seiber, J. Appl. Phys. 44, 3394 (1972).
[10]E. H. Gregory, Ph.D. thesis, University of California at Los Angeles, 1965.
[11]E. H. Gregory and H. E. Bömmel, Phys. Rev. Lett. 15, 404 (1965).
[12]D. G. Westlake, T. H. Wang, R. K. Sundfors, P. A. Fedders,

and D. I. Bolef, Phys. Status Solidi A 25, K35 (1974).
[13]B. Ströbel, K. Läuger, and H. E. Bömmel, *Magnetic Resonance and Related Phenomena,* Proceedings of the XXth Congrès Ampère, Tallinn, 1978, edited by E. Kundla, E. Lippmaa, and T. Saluvere (Springer, New York, 1979).
[14]D. G. Westlake and S. T. Ockers, J. Less-Common Met. 42, 255 (1975).
[15]T. Schober, in *Proceedings of the 2nd International Congress on Hydrogen in Metals, Paris, 1977* (Pergamon, New York, 1978), Sec. 1D2, Vol. 2.
[16]P. A. Fedders, Phys. Rev. B 11, 995 (1975).
[17]P. A. Fedders, Phys. Rev. B 14, 4221 (1976).
[18]N. Bloembergen, *Report of the Conference on Defects in Crystalline Solids, Bristol, 1954* (Physical Society, London, 1955), p.1.
[19]R. Bersohn, J. Chem. Phys. 20, 1505 (1952).
[20]R. K. Sundfors, Phys. Rev. 185, 458 (1969).
[21]R. K. Sundfors, T. H. Wang, D. I. Bolef, Peter A. Fedders, and D. G. Westlake, Phys. Rev. B 12, 26 (1975).
[22]B. Ströbel and V. Müller, Phys. Rev. B 24, 6292 (1981).
[23]N. Asano, Y. Ishikawa, and M. Hirabayashi, J. Appl. Cryst. 11, 681 (1978).
[24]D. G. Westlake, Scr. Metall. 11, 689 (1977).