PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

Anisotropy of the electron momentum distributions in $NbH_{0.29}$

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(Received 16 July 1976)

Anisotropies of the Compton profiles of α-phase $NbH_{0.29}$ have been measured. A reduction in the measured anisotropy compared to pure Nb is interpreted as evidence that the hydrogen donates its electron to the Nb conduction band.

I. INTRODUCTION

The study of hydrogen in metals is a subject of current interest due to both a desire to gain a fundamental understanding of gases dissolved in metals and the possible use of metals as a storage medium in hydrogen-related energy systems. A basic question in hydrogen-metal solutions is the electronic state assumed by the hydrogen. Two models have been proposed; the hydrogen atom can either donate its electron to the conduction band of the host metal (the protonic model) or it can remove an electron from the conduction band and form an anion with bound 1s states (anionic model).[1]

Although a number of measurement techniques provide information about the electronic state of the hydrogen, a measurement of the electron momentum density by Compton scattering provides a direct and sensitive probe. This is partly because Compton scattering is particularly sensitive to the electronic states of the valence electrons and is insensitive to the lattice distortions introduced in the process of charging the metal with hydrogen. In a previous study, McIntire and Batterman[2] compared their measured Compton profiles of polycrystalline vanadium hydride ($VH_{0.45}$) to a free-electron-atomic-core model and concluded that the protonic model is valid. In a more recent study Pattison *et al.*[3] measured the Compton profile of a [110] crystal of niobium deuteride ($NbD_{0.6}$) and after comparing the profile with calculations of both the protonic and anionic models of Nb concluded that the protonic model is valid.

In this paper we report the measurements of the anisotropy of the momentum distribution of $NbH_{0.29}$ and show that the anisotropy is very sensitive to the addition of hydrogen. We conclude, as in the previous studies, that the protonic model is valid for the niobium hydrides and the hydrogen electrons are donated to the niobium conduction band.

II. EXPERIMENTAL DETAILS

A. Sample preparation

The sample was prepared by heating a high-purity single-crystal rod of electron-beam zone-refined niobium to 400 °C and introducing the hydrogen at about 73 Torr,[4] by means of a temperature-controlled hydrogen atmosphere system which contained a titanium getter. The [110] crystallographic axis was aligned to within 2° of the rod axis. After cooling, a piece of the rod was removed for analysis and the remainder, 0.64 cm in diameter and 3.18 cm long, was mounted in the Compton spectrometer. After the Compton measurements were completed a piece of the sample was reanalyzed for hydrogen. Both analyses showed the sample to be $NbH_{0.29}$.

B. Experimental apparatus and data processing

The Compton measurements were made on a γ-ray spectrometer described in Ref. 5. The γ-ray source was $^{123}Te^{m}$ and the photons scattered at an angle of 173° were energy analyzed with a Ge(Li) detector.

The niobium-hydrogen phase diagram[1] has a two-phase region where niobium and niobium hydride coexist. At 20 °C this two-phase region extends from ~0.03 to ~0.62 at.% hydrogen. In order to maintain a homogeneous solution at 0.29 at.% H it was necessary to heat the sample to 200 °C in H_2 during measurement. This was accomplished by placing the sample in an aluminum shroud[6] (Fig. 1). The sample was attached to the base and oriented such that the scattering vector was along either the [100], [110], or [111] axis. The cover was then attached and H_2 gas placed in the interior. During the measurement the spectrometer chamber was evacuated and the shroud and sample were kept at 200 ± 10 °C.

Compton profiles were measured for the [100],

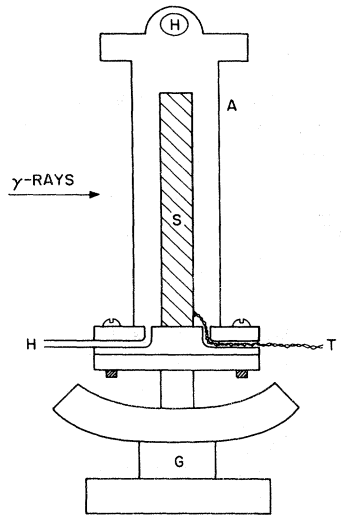

FIG. 1. Sample mount and Al shroud. A: thin-walled Al tube; S: sample; H: H_2 gas inlet; T: thermocouple; G: goniometer.

[110], and [111] directions for the $NbH_{0.29}$ and for the [100] and [110] directions for pure Nb. Approximately 2.5×10^4 counts were collected at the profiles center. The Nb was measured without the Al shroud so that the Nb data could be compared with theoretical calculations and so a correction for the shroud could be made to the $NbH_{0.29}$ data. The raw profiles for each direction were processed as described in Ref. 5. To correct for the Al shroud, the difference between the [110] directions for the Nb and $NbH_{0.29}$ was used. This correction need not be particularly accurate since it only corrects for the size of the anisotropy and does not affect its shape. The correction in the peak-to-peak amplitude of the anisotropy at $q=0$ was less than 2%. Since the multiple scattering should be similar in both the Nb and $NbH_{0.29}$, no correction was made for this effect.

The profiles were normalized[7] such that the integral of the profile from $q=0$ to 15 a.u. equaled 19.421 electrons for Nb and equaled 19.566 for the $NbH_{0.29}$. No correction was made for the finite resolution of the spectrometer to the experimental data, but the theoretical profiles were convoluted with a Gaussian with $\sigma=0.202$.

The theoretical profiles for Nb were obtained by taking the calculations of Wakoh *et al.*[8] for the five valence electrons and adding them to a

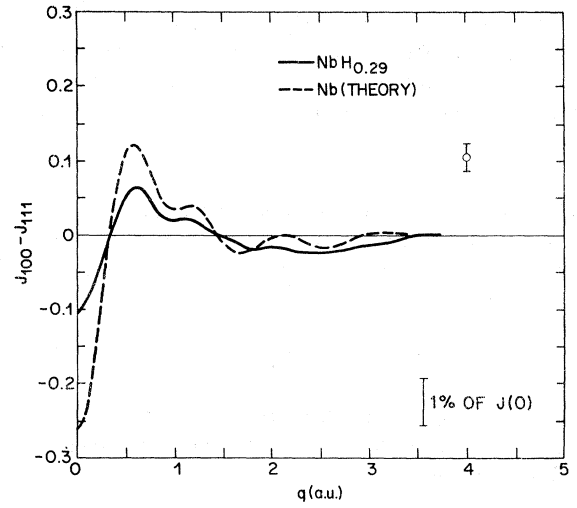

FIG. 3. $J_{100}-J_{111}$ anisotropy: (solid line) $NbH_{0.29}$, (dashed line) Nb, theory.

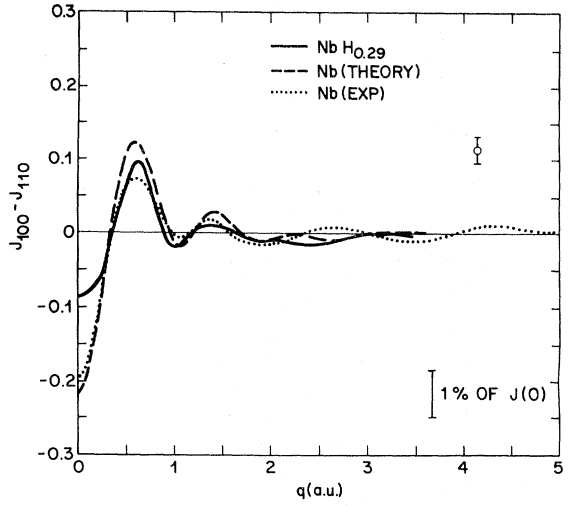

FIG. 2. $J_{100}-J_{110}$ anisotropy: (solid line) $NbH_{0.29}$, (dashed line) Nb, theory; (dotted line) Nb, experiment.

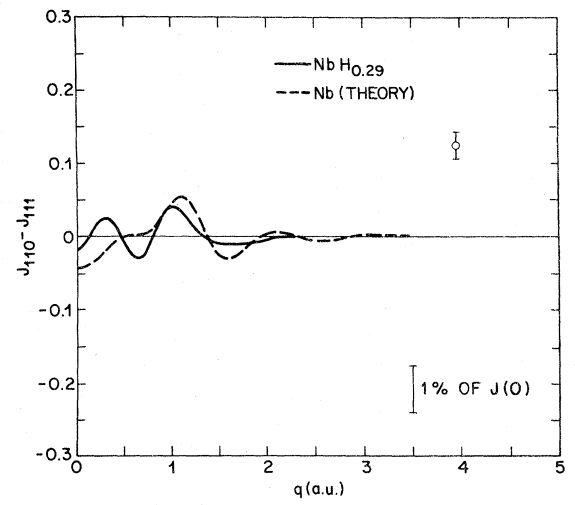

FIG. 4. $J_{110}-J_{111}$ anisotropy: (solid line) $NbH_{0.29}$, (dashed line) Nb, theory.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ core calculated by Biggs *et al.*[9] The profiles were checked for the correct normalization and then convoluted with the experimental resolution function.

III. THEORY

Since the theory for Compton scattering has been previously given[5] it will not be repeated here. Only the key relations will be stated. The Compton profile is defined as

$$J(q) = \int_{-\infty}^{\infty} \chi(\vec{p})\chi^*(\vec{p})\, dp_\alpha\, dp_\beta ,$$

where $\chi(\vec{p})$ is the electronic momentum wave function, q is the magnitude of the momentum along the scattering vector, i.e.,

$$q = \vec{k}\cdot\vec{p}/|k| ,$$

and the directions α and β are perpendicular to the scattering vector. The normalization condition on the profiles is given by

$$\int_0^{\infty} J(q)\, dq = \tfrac{1}{2}N ,$$

where N is the number of electrons per formula unit. The relation between the energies of the incident (E_0) and scattered (E) photons and q is

$$q = mc\,\frac{E_0 - E - E_0 E(1-\cos\theta)/mc^2}{(E_0^2 + E^2 - 2E_0 E\cos\theta)^{1/2}} ,$$

where θ is the scattering angle.

IV. RESULTS AND DISCUSSION

The measured anisotropies of $NbH_{0.29}$ are shown in Figs. 2–4. Also included in these figures are the anisotropies of Nb calculated by Wakoh *et al.*,[8] and in Fig. 2, the experimental anisotropy for Nb. The data are tabulated in Table I.

The $J_{100} - J_{110}$ anisotropy measured experimentally for Nb is in good agreement with the theoretical anisotropy. The maxima and minima occur at the same values of q and only the peak at $q \sim 0.6$

TABLE I. Measured anisotropy of $NbH_{0.29}$ and Nb.[a]

q (a.u.)	Nb ⟨100⟩ − ⟨110⟩	⟨100⟩ − ⟨110⟩	$NbH_{0.29}$ ⟨100⟩ − ⟨111⟩	⟨110⟩ − ⟨111⟩
0.0	−0.195	−0.086	−0.105	−0.019
0.1	−0.177	−0.080	−0.089	−0.010
0.2	−0.115	−0.068	−0.058	0.010
0.3	−0.038	−0.044	−0.020	0.024
0.4	0.025	0.001	0.019	0.018
0.5	0.062	0.055	0.050	−0.005
0.6	0.073	0.091	0.064	−0.027
0.7	0.064	0.085	0.058	−0.028
0.8	0.042	0.044	0.038	−0.005
0.9	0.016	−0.000	0.023	0.024
1.0	−0.003	−0.019	0.019	0.038
1.1	−0.006	−0.012	0.022	0.034
1.2	0.004	0.002	0.020	0.018
1.3	0.015	0.009	0.011	0.002
1.4	0.018	0.010	0.003	−0.008
1.5	0.009	0.008	−0.003	−0.012
1.6	−0.002	0.003	−0.009	−0.012
1.7	−0.011	−0.004	−0.015	−0.011
1.8	−0.014	−0.010	−0.020	−0.010
1.9	−0.015	−0.011	−0.019	−0.008
2.0	−0.015	−0.010	−0.017	−0.004
2.1	−0.012	−0.011	−0.018	0.000
2.2	−0.008	−0.013	−0.021	0.001
2.3	−0.002	−0.015	−0.023	0.001
2.4	0.003	0.016	−0.024	0.000
2.5	0.007	−0.015	−0.023	0.001
2.6	0.009	−0.012	−0.022	0.001
2.7	0.009	−0.010	−0.021	−0.000
2.8	0.007	−0.006	−0.018	−0.001
2.9	0.004	−0.003	−0.016	−0.001
3.0	0.001	−0.001	−0.014	−0.001

[a] Data are not corrected for spectrometer resolution function.

is smaller in the experiment than predicted by the theory. This comparison gives us confidence that the theoretical curves do indeed represent Nb and we can compare them with the $NbH_{0.29}$ anisotropy.

From Figs. 2–4 it is clear that the amplitude of the anisotropy of the hydride is in all cases reduced compared to the anisotropy of Nb and is qualitatively different, although the $J_{110} - J_{111}$ anisotropy is almost within the error bars. Thus the dissolved hydrogen is affecting the momentum anisotropy of the host Nb. The question is whether the change in anisotropy is due to the hydrogen giving or taking an electron from the Nb conduction band.

A detailed comparison with theory is not possible at present since no calculation for the hydride has been published. However an analysis of the band structure calculations of Nb by Mattheiss[10] and the Compton-profile calculations of Wakoh *et al.*[8] does provide some qualitative answers. The Fermi surface[10] of Nb is characterized by a large "jungle gym" of third zone holes centered on Γ with the arms along the [100] directions, and third zone hole ellipsoids centered at N on the zone face. These holes are seen in the Compton profile for J_{100} as a dip at $0 < q < 0.5$ a.u.[11] A slice through the Brillouin zone at Γ and perpendicular to [100] encounters relatively few filled states. If the addition of hydrogen to Nb raises the Fermi level, these hole surfaces will shrink, the dip in the J_{100} profile will decrease, the $J_{100} - J_{110}$ and $J_{100} - J_{110}$ anisotropies will become smaller and the $J_{110} - J_{111}$ anisotropy will remain relatively unaffected. Since this is what we observe experimentally, we conclude that the hydrogen has donated its electron to the Nb conduction band and the protonic model is valid for this hydride.

ACKNOWLEDGMENTS

We would like to thank S. Wakoh for making available to us the details of his Compton-profile calculations, H. Levie for designing and building the sample shroud, and A. J. Ehlert for growing the crystal.

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