Lattice Dynamics of Tantalum

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(Received 22 May 1964)

The frequency–wave-vector dispersion relation ($\nu(\mathbf{q})$) for lattice waves traveling in the [00ζ], [$\zeta\zeta$0], and [$\zeta\zeta\zeta$] symmetric directions of tantalum has been measured at 296°K, using methods of neutron inelastic scattering. The results show strong similarities with the previously measured $\nu(\mathbf{q})$ for niobium. The results can be fitted by a Born–von Kármán force model only if very long-range forces are invoked. Because of the peculiar nature of $\nu(\mathbf{q})$, the Debye approximation appears to be better for tantalum than for most other materials.

INTRODUCTION

INTEREST in the lattice dynamics of tantalum stems from measurements which were previously carried out on other body-centered cubic transition metals. For niobium,[1] $\nu(\mathbf{q})$ shows some very unusual features; for example, the crossing of the longitudinal (L) and transverse (T) branches in the [00ζ] direction; except when demanded by symmetry, such behavior had not previously been observed for any other metal. On the other hand, measurements of $\nu(\mathbf{q})$ for tungsten[2] and molybdenum[3] show radically different behavior, and in these cases many features of the experimental results are reasonably well reproduced by a third neighbor Born–von Kármán axially symmetric force model.[4] The present studies of tantalum are part of a series of similar experiments which are designed to see if there is any pattern in the lattice dynamical properties of the body-centered cubic metals in columns V and VI of the periodic table; if any such pattern can be established, it may be possible to find some correlation with other perplexing properties of the transition metals; for example, the observed pattern of the superconducting transition temperatures.[5]

EXPERIMENTAL RESULTS

The frequency–wave-vector dispersion relation $\nu(\mathbf{q})$, for lattice waves traveling in the symmetric directions [00ζ], [$\zeta\zeta$0], and [$\zeta\zeta\zeta$], or, in group-theory notation Δ, Σ, and Λ, respectively, have been determined for tantalum at 296°K. The experiment was carried out using the triple-axis neutron spectrometer[6] in its constant **Q** mode of operation and with variable incident neutron energy. For most of the experiments, the analyzing spectrometer was set to observe neutrons of energy 0.0226 and 0.0255 eV. The specimen consisted of three single crystals (obtained from Materials Research Corporation) each 5 cm long and about 1 cm in diameter. The (1$\bar{1}$0) plane was perpendicular to the cylindrical axis which was mounted vertically. Each of the three crystals could be oriented independently and their alignment was carried out by means of neutron diffraction. The measured mosaic spread of the (222) plane measured in the (approximately) parallel position against a germanium single crystal was about 0.15 deg. The measured modes for the Δ, Σ, and Λ directions are shown in Fig. 1 and tabulated in Table I. Many of the qualitative features of these results are similar to those previously observed for niobium. For example, the Δ L and T branches are observed to cross at $\zeta\approx0.7$ and the tendency for the Δ and Σ transverse branches to avoid normal dispersive behavior is apparent. However, these features do not appear to be as pronounced in tantalum as they are in niobium.

In addition to measuring the dispersion curves shown in Fig. 1, it is also possible to observe, in the (1$\bar{1}$0) plane, the end point of the other transverse branch (T_1) for the Σ direction. [In order to obtain measurements for the whole branch, it is necessary to change the crystal orientation so that a (100)-type plane is horizontal.] This mode, designated as $(\frac{1}{2},\frac{1}{2},0)T_1$, has been included in Table I. It should be noticed that, unlike the case for niobium, the ΣT_1 and ΣT_2 branches apparently do not intersect in tantalum. The reason for this behavior is that in tantalum the elastic constant[7]

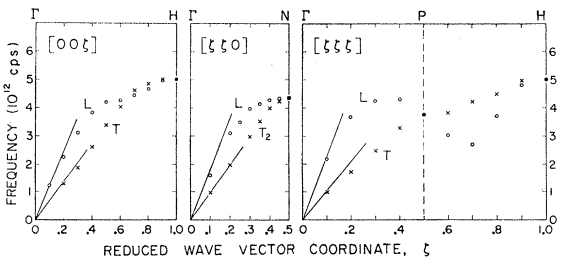

FIG. 1. The measured dispersion curves for the high symmetry directions in tantalum at 296°K. The solid points are modes which are required to be triply degenerate by symmetry. The solid lines through the origins have been calculated from the measured elastic constants.

[1] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters **11**, 271 (1963); Phys. Chem. Solids (to be published).
[2] S. H. Chen and B. N. Brockhouse, Solid-State Commun. **2**, 73 (1964).
[3] S. H. Chen and A. D. B. Woods, Bull. Am. Phys. Soc. **9**, 83 (1964).
[4] G. W. Lehman, T. Wolfram, and R. E. De Wames, Phys. Rev. **128**, 1593 (1962).
[5] For a general review see B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).
[6] B. N. Brockhouse in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1960), p. 113.
[7] D. I. Bolef, J. Appl. Phys. **32**, 100 (1961); F. H. Featherston and J. R. Neighbours, Phys. Rev. **130**, 1324 (1963).

TABLE I. Frequencies of observed modes in tantalum at 296°K.

	$\nu(10^{12}$ cps)			
ζ	$[00\zeta]L$	$[00\zeta]T$	$[\zeta\zeta\zeta]L$	$[\zeta\zeta\zeta]T$
0.10	1.23±0.06	···	2.24±0.05	0.98±0.04
0.20	2.28±0.05	1.28±0.04	3.75±0.07	1.73±0.04
0.30	3.10±0.05	1.88±0.04	4.38±0.10	2.48±0.04
0.40	3.82±0.06	2.60±0.04	4.30±0.08	3.28±0.05
0.50	4.20±0.08	3.37±0.05	3.78±0.06	3.78±0.06
0.60	4.25±0.08	4.03±0.07	3.03±0.06	3.80±0.10
0.70	4.45±0.08	4.63±0.08	2.70±0.06	4.20±0.15
0.80	4.68±0.08	4.85±0.08	3.70±0.10	4.48±0.15
0.90	4.98±0.10	5.03±0.08	4.78±0.10	4.90±0.10
1.00	5.03±0.07	5.03±0.07	5.03±0.07	5.03±0.07

	$\nu(10^{12}$ cps)		
ζ	$[\zeta\zeta 0]L$	$[\zeta\zeta 0]T_1$	$[\zeta\zeta 0]T_2$
0.10	1.65±0.10	···	0.96±0.04
0.20	3.10±0.10	···	1.95±0.04
0.25	3.51±0.07	···	···
0.30	3.95±0.08	···	2.97±0.05
0.35	4.15±0.08	···	3.51±0.05
0.40	4.24±0.08	···	3.97±0.06
0.41	4.28±0.08	···	···
0.45	4.32±0.08	···	4.24±0.06
0.50	4.35±0.08	2.63±0.08	4.35±0.06

C_{44} is greater than $(C_{11}-C_{12})/2$ whereas in niobium C_{44} is less than $(C_{11}-C_{12})/2$.

The present experiment was not designed to detect any sharp anomalies in the dispersion curves, such as those which might be caused by the Kohn effect.[8]

DISCUSSION

Attempts have been made to fit these results using a Born–von Kármán force-constant model, and to compare the force constants obtained with the results of similar fitting to $\nu(\mathbf{q})$ measurements of niobium, molybdenum, and tungsten. Fourier analysis of the individual dispersion curves,[9–11] in the form

$$4\pi^2 M\nu^2=\sum_{n=1}^{N}\Phi_n[1-\cos(\pi\zeta/\zeta_{\max})],$$

where $\zeta_{\max}$ is a function of the particular branch, indicates that the forces are of long range, and furthermore, that the values of the Fourier coefficients Φ_n are very similar to the Φ_n for niobium.

A direct linear least-squares fit to the measured $\nu(\mathbf{q})$ does not result in a satisfactory model for tantalum. A similar fit to the niobium data[1] with 23 parameters yielded an eighth-neighbor Born–von Kármán force constant model which reproduced the measured $\nu(\mathbf{q})$ reasonably well. Because fewer branches were measured for tantalum, it was not possible to fit an eighth-neighbor general force model to the data. A seventh-neighbor (19 parameter) fit was carried out however. In addition, an axially symmetric (A-S) force model[5] with interactions out to tenth neighbors [at positions (333) and (511) in units of $a/2$] was fitted to the data; this model had twenty parameters. The calculated force constants are shown in Table II. The values of many of these force constants are very sensitive to the model used. During the course of the analysis, it was noticed that the ΣT_2 branch, particularly for modes with $\zeta>0.3$, had a strong influence on the calculated force constants; the value of α_2 (the notation is that given in Ref. 11) in the eighth-neighbor A-S fit was -1654 dyn/cm with the fit made to all of the data, and $+7953$ dyn/cm when the four phonons on this branch with $\zeta>0.3$ were omitted.

In view of such pecularities in the tantalum results, the analysis of the niobium data was re-examined. The values of the calculated force constants for niobium did not appear to vary significantly with the number of neighbors considered, but, the exclusion of the ΣT branches resulted in unstable ninth- and tenth-neighbor A-S models; the *calculated* frequency of the T_2 mode at N was imaginary. The use of these complicated force models with strong long-range forces to calculate the

TABLE II. Born–von Kármán force constants (units dyn/cm) for seventh-neighbor general and tenth-neighbor axially symmetric force models. (See Ref. 11 for notation.)

Position of neighbor	Force constant	Seventh-neighbor general model	Tenth-neighbor A-S model
(1,1,1)$a/2$	α_1	16983	16762
	β_1	11201	11433
(2,0,0)$a/2$	α_2	1182	−915
	β_2	1423	320
(2,2,0)$a/2$	α_3	3546	1470
	β_3	−5427	−2672
	γ_3	1943	$\alpha_3-\beta_3$
(3,1,1)$a/2$	α_4	3577	3337
	β_4	−718	275
	γ_4	−1728	$(\alpha_4-\beta_4)/8$
	δ_4	983	$3(\alpha_4-\beta_4)/8$
(2,2,2)$a/2$	α_5	−493	−571
	β_5	812	−2162
(4,0,0)$a/2$	α_6	−3705	−888
	β_6	134	−3178
(1,3,3)$a/2$	α_7	558	−1003
	β_7	−237	−469
	γ_7	106	$-9(\alpha_7-\beta_7)/8$
	δ_7	−683	$-3(\alpha_7-\beta_7)/8$
(4,2,0)$a/2$	α_8	···	1379
	β_8	···	394
	γ_8	···	$-(\alpha_8-4\beta_8)/3$
	δ_8	···	$2(\alpha_8-\beta_8)/3$
(4,2,2)$a/2$	α_9	···	−739
	β_9	···	572
	γ_9	···	$(\alpha_9-\beta_9)/3$
	δ_9	···	$2(\alpha_9-\beta_9)/3$
(3,3,3)$a/2$	α_{10}	···	33
	β_{10}	···	−301
(5,1,1)$a/2$	α_{11}	···	$\alpha_{10}+16\beta_{10}/9$
	β_{11}	···	$\alpha_{10}-8\beta_{10}/9$
	γ_{11}	···	$\beta_{10}/9$
	δ_{11}	···	$5\beta_{10}/9$

[8] W. Kohn, Phys. Rev. Letters **2**, 393 (1959).
[9] A. J. E. Foreman and W. M. Lomer, Proc. Phys. Soc. (London) **B70**, 1143 (1957).
[10] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).
[11] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).

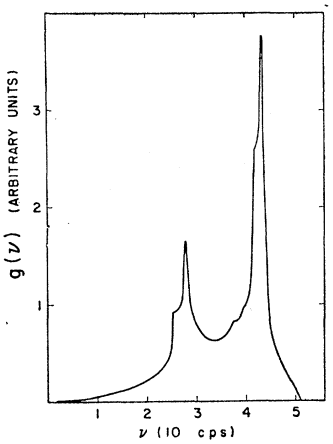

FIG. 2. The frequency distribution function for tantalum calculated from the seventh-neighbor general force model fitted to the data of Fig. 1.

frequencies of unobserved normal modes, and hence, to obtain frequency distribution functions,[1,12,13] should therefore be treated with caution. The use of such a procedure for materials in which the long-range forces are relatively weak (e.g., sodium) or well-known (alkali halides) is probably safer; such a conclusion has been borne out by comparison of calculated and observed nonsymmetric modes in these materials.[11,14]

In spite of the doubtful validity of such a model, the seventh-neighbor general force model was used to calculate the frequency distribution function $g(\nu)$; the result is shown in Fig. 2. Calculation of the frequencies of unmeasured modes using this model did not indicate unrealistic values for any of the frequencies. The Debye approximation appeais to be rather better for tantalum than for most other materials. This is probably a reflection of the tendency for the Δ and Σ transverse branches to resist dispersion.

CONCLUSIONS

The measured $\nu(\mathbf{q})$ for tantalum shows some striking resemblances with the $\nu(\mathbf{q})$ for niobium, a fact borne out by the similarity of the interplanar force constants Φ_n as determined by Fourier analysis of the individual dispersion curves. This similarity appears to break down when individual force constants are compared but this may be essentially a mathematical difficulty, caused by the large number of force constants involved. The main differences between the $\nu(\mathbf{q})$ for these two metals appears to be in the transverse branches for the Δ and Σ directions which, in the long-wavelength limit, are determined by the elastic constant C_{44}. This elastic constant appears to be anomalously low for niobium and the phonons of shorter wavelength must counteract this by exhibiting "negative dispersion" in order to satisfy the symmetry conditions at the point H.

It would be very desirable to have measurements of $\nu(\mathbf{q})$ for vanadium for comparison with the present results, particularly since the measured $g(\nu)$ for vanadium[15] hints that $\nu(\mathbf{q})$ may contain some very peculiar features. Because the coherent neutron scattering cross section for vanadium is so small ($\sim$0.03 b), such a measurement is impossible using neutrons. It should be feasible, however, using x rays, particularly since much information is already available from the measured $g(\nu)$ and from extrapolation of $\nu(\mathbf{q})$ for niobium and tantalum.

It is difficult at this stage to draw any conclusions about the validity of the proposed axially symmetric model[5] for the transition metals. Imposition of the conditions of this model gives a similar fit to that obtained with the general force model, provided that the range of the forces is increased to give approximately the same number of independent parameters. With such a large number of independent parameters, neither of these models is physically realistic; a more fundamental approach is necessary if the lattice dynamics of these metals is to be understood.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance of Dr. G. Dolling in carrying out these measurements and to express his thanks to Dr. Dolling and Dr. G. Gilat for the use of their computer program to carry out calculations of $g(\nu)$. E. A. Glaser and A. Bell gave valuable technical assistance.

[12] A. E. Dixon, A. D. B. Woods, and B. N. Brockhouse, Proc. Phys. Soc. (London) **81**, 973 (1963).

[13] G. Gilat and G. Dolling, Phys. Letters **8**, 304 (1964).

[14] R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, Phys. Rev. **131**, 1030 (1963).

[15] At least five independent measurements have been made: A. T. Stewart and B. N. Brockhouse, Rev. Mod. Phys. **30**, 250 (1958); C. M. Eisenhauer, I. Pelah, D. J. Hughes, and H. Palevsky, Phys. Rev. **109**, 1046 (1958); K. C. Turberfield and P. A. Egelstaff, *ibid.* **127**, 1017 (1962); M. G. Zemlyanov, Yu. M. Kagan N. A. Tchernoplekov, and A. G. Tchetserin, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 125; R. Haas, W. Kley, K. H. Krebs, and R. Rubin, *ibid.*, p. 145.