Investigation of the Phonon Dispersion Relations of Chromium by Inelastic Neutron Scattering*

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(Received 8 April 1971)

The phonon dispersion relations for chromium have been measured at room temperature in three symmetry directions using the triple-axis neutron diffractometer at the Missouri University Research Reactor. Careful consideration was given to focusing techniques associated with instrumental resolution. Consequently, the most appropriate experimental configuration, leading to the most favorable focusing criteria, was used for each phonon measurement. The experimentally determined phonon dispersion relations for chromium showed at least four regions of anomalous behavior not previously observed. The regions of anomalous behavior are shown to be related to the structure of the Fermi surface of chromium in agreement with recent band-structure calculations. A fourth-nearest-neighbor Born–von Kármán analysis of the dispersion relations has been used to calculate the frequency distribution function for chromium.

INTRODUCTION

The transition metals, chromium, molybdenum, and tungsten, are each body-centered cubic with one atom per unit cell. Thus, the general shape of the phonon dispersion curves of these metals is quite similar. Moreover, they have similar electronic properties and, consequently, similar Fermi surfaces, as first pointed out by Lomer.[1] Certain features of the Fermi surface may give rise to anomalous behavior in the phonon dispersion relations. Thus, one might expect to observe similar anomalous behavior in the phonon dispersion relations of these three transition metals. However, molybdenum and tungsten are nonmagnetic while chromium is antiferromagnetic with a Néel temperature of 311 °K. The antiferromagnetic state of chromium is critically dependent on the electronic band structure and, hence, is also related to the prominent features of the Fermi surface. Thus, it is of interest to compare a careful experimental determination of the phonon dispersion relations of chromium with those of tungsten and molybdenum in order to gain information related to the similarities and/or differences of their Fermi surfaces.

DISCUSSION AND RESULTS

Kohn[2] first showed that the interaction between the conduction electrons and the lattice vibrations may give rise to an observable anomaly in the phonon dispersion relations. This anomalous behavior occurs at a phonon wave vector equal to an extremal dimension of the Fermi surface. These Kohn anomalies have been observed in the phonon dispersion relations of several metals.[3–5] It has also been shown[6] that the interaction between the conduction electrons and the lattice vibrations may give rise to anomalous behavior in the phonon dispersion relations at a phonon wave vector which separates two parallel portions or "nesting" portions of the Fermi surface. Thus anomalies in the phonon dispersion relations may be identified with both extremal dimensions and nesting portions of the Fermi surface.

The band-structure calculations of Lomer[1] and Loucks[7] indicate similar Fermi surfaces among paramagnetic chromium, molybdenum, and tungsten. Consequently, one would expect similar anomalous behavior to exist in the phonon dispersion relations of each metal. Woods and Chen[5] and Powell *et al.*[8] have measured the phonon dispersion relations of molybdenum and observed striking anomalies near the N and H symmetry points which can be identified with the nesting property of the Fermi surface. Anomalous behavior in the phonon dispersion relations of tungsten has been predicted theoretically,[9] and the phonon dispersion relations have been measured experimentally by Chen and Brockhouse.[10] The data, however, are too sparse to clearly demonstrate any anomalous behavior, except perhaps near the N symmetry point measured in the [011] direction.

The early data for the phonon dispersion relations of chromium, measured by Møller and Mackintosh,[11] are also too sparse to clearly identify anomalous behavior. However, like tungsten, anomalous behavior near the N symmetry point is suggested. Thus a careful experimental determination of the phonon dispersion relations of chromium in three directions of high symmetry and at room temperature has been undertaken, to see if the expected anomalous behavior can be observed.

The experimental results for the phonon dispersion relations of chromium measured in the [001], [011], and [111] directions are shown in Fig. 1. For each neutron group in each branch of the dispersion relations, careful consideration was given

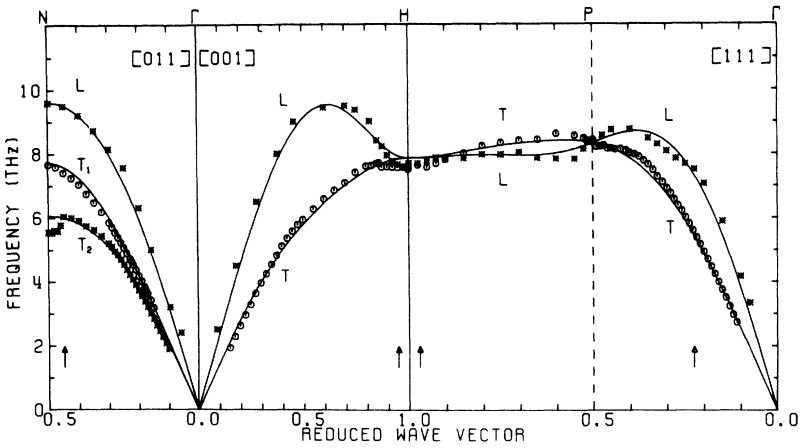

FIG. 1. Phonon dispersion relations of chromium at room temperature. The solid line represents a fourth-nearest-neighbor Born–von Kármán analysis of the experimental data.

to focusing criteria arising from the characteristic resolution of a triple-axis neutron diffractometer.[12] Thus, well-defined neutron groups were observed and, as a result, the total experimental error is on the order of 2%. The results of a resolution calculation which includes the mosaic spread of the sample with substantiating experimental resolution data will be published directly.

The data indicate four regions of anomalous behavior, not identified by earlier work on chromium.[11] First, a striking depression near the N symmetry point is apparent in the transverse two branch measured in the [011] direction. Second, there is a depression in the dispersion relation, near the H symmetry point, in the transverse branch measured in the [001] direction. Third, a change in the slope of the dispersion curve is observed near $q = 0.25$ (reduced units) in the longitudinal branch measured in the [111] direction. Fourth, an abrupt change in the frequency is observed near the P symmetry point of the transverse branch measured in the [111] direction.

The region of anomalous behavior, near the N symmetry point, can be identified with nesting portions of the Fermi surface. Figure 2 shows the [011] section of the Fermi surface of paramagnetic chromium taken from the band-structure calculations of Asano and Yamashita.[13] The line DE of Fig. 2 connects nesting portions of the Fermi surface, and the length of DE indicates that the anomaly might occur at a phonon wave vector equal to about 0.46 (reduced units) in the [011] direction in agreement with the present data. Earlier band-structure calculations of Loucks[7] did not show the hole pockets centered at N for paramagnetic chromium, but did show such hole pockets for tungsten and molybde-

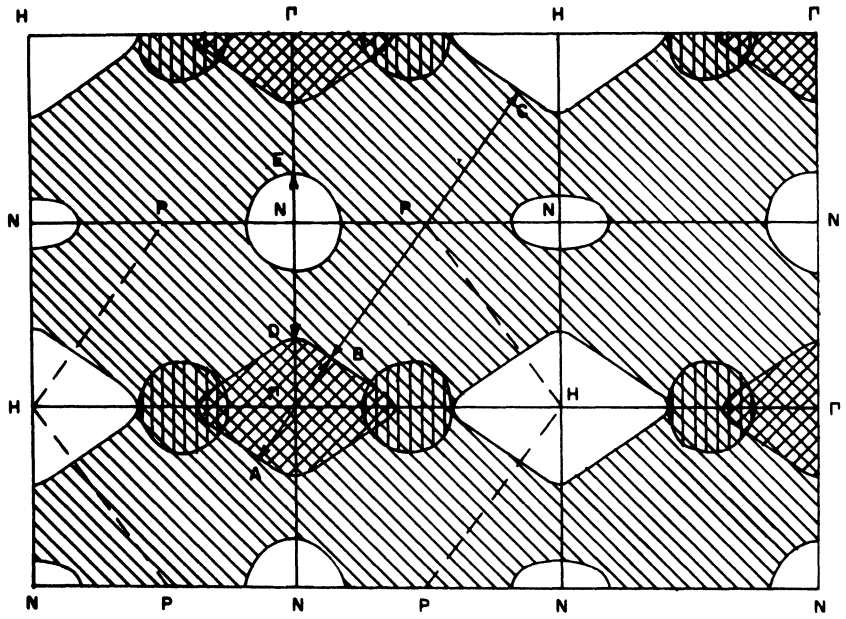

FIG. 2. [011] projection of the Fermi surface of chromium from the calculations of Asano and Yamashita.

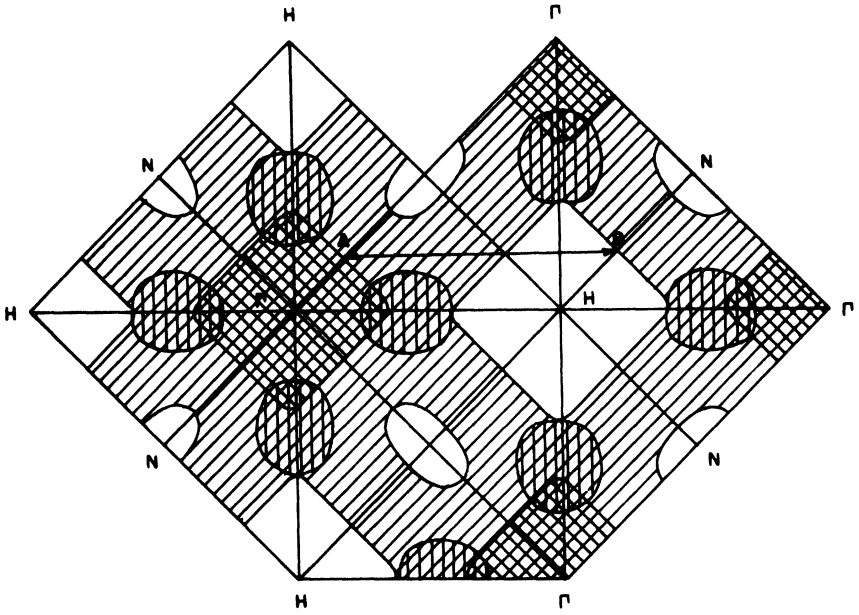

FIG. 3. [001] projection of the Fermi surface of chromium from the calculations of Asano and Yamashita.

num. In the absence of a hole pocket at N for chromium, it would be impossible to account for the anomalous behavior of the dispersion relation in this region in terms of band structure. Consequently, the data tend to support the existence of the hole pockets at N, and suggest that the similar behavior of the dispersion relations for tungsten, molybdenum, and chromium in the region near N ([011] direction) is due to the similarity of their Fermi surfaces. The recent band-structure calculations of Connolly[14] indicate and the experimental work of Graebner and Marcus[15] definitely demonstrate the existence of the hole pockets centered at N for chromium.

The region of anomalous behavior near the H symmetry point can also be attributed to nesting portions of the Fermi surface. Figure 3 shows the [001] projection of the Fermi surface of chromium. The line AB in Fig. 3 and the line AC in Fig. 2 correspond to nesting portions of the Fermi surface which could give rise to anomalous behavior near the H symmetry point as measured in the [001] and [111] directions, respectively. The length of AB corresponds to a wave vector of about 0.96 (reduced units) in the [001] direction while the length of AC corresponds to a wave vector of about 0.98 (reduced units) in the [111] direction. At the H symmetry point all modes are degenerate. Thus, anomalous behavior near H in both directions should be demonstrated by all modes. Among the measured branches near H, only the transverse branch in the [001] direction has a positive slope in this region. Consequently, an anomalous depression in the frequency near H would be more apparent in this branch, in agreement with the present data.

Figure 4 shows an enlargement of the data for the longitudinal and transverse branches in the [001] and [111] directions near the H symmetry point. The error bars are plus and minus twice the standard deviation and represent an error of approximately 2%. The solid line is simply a guide to the eye. If the transverse branch in the [001] direction were extrapolated from $q = 0.85$ (reduced units) to the zone boundary, it would intersect the zone boundary at a frequency of about 7.83 THz. If the longitudinal branch in the [111] direction were also extrapolated from $q = 0.925$ (reduced units) to the zone boundary, it would also intersect the zone boundary at this same frequency. The dashed lines in Fig. 4 represent a possible extrapolation for all branches and tend to emphasize the anomalous behavior in

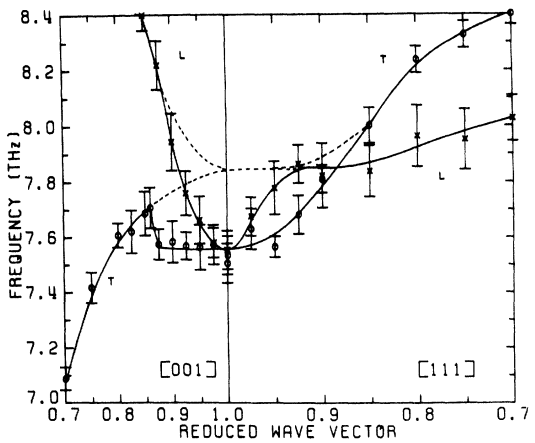

FIG. 4. Detailed representation of the behavior of the phonon dispersion relations near the H symmetry point.

all modes degenerate at H. In comparing these results for chromium (Fig. 4) with the dispersion relations of molybdenum, one notices a strong similarity in the anomalous behavior near the H symmetry point.

Since the experiment was conducted at room temperature (300 °K), one must also consider the antiferromagnetic property of chromium. The magnetic structure is incommensurate with the lattice structure. Thus, the origin of the spin-wave dispersion relation does not occur at the zone boundary, but rather at a wave vector of $q = 0.96$ (reduced units) in the [001] direction.[16] The slope of the spin-wave dispersion relation is extremely steep[17] and hence, it is possible to have a magnon-phonon interaction, near the H symmetry point, where the two branches cross. However, for such a steep magnon dispersion relation and a constant momentum mode of scan, the magnon dispersion relation would not be expected to distort the phonon groups, but rather simply contribute to an essentially constant background. Since similar anomalous behavior near H is observed in nonmagnetic molybdenum, it is assumed that the observed behavior in chromium near H is due to nesting portions of the Fermi surface rather than magnon-phonon interactions.

The line AB in Fig. 2 corresponds to an extremal dimension of the Fermi surface with a reduced wave vector of the order of 0.25 (reduced units) in the [111] direction. Thus the anomalous behavior in this region demonstrated by the longitudinal branch measured in the [111] direction may be identified with this extremal dimension of the Fermi surface. The apparent anomaly near the P symmetry point does not correspond to either an extremal dimension or a nesting portion of the Fermi surface. Consequently this behavior is not understood in terms of present band-structure calculations.

It is of interest to consider other anomalies which might be expected from a further consideration of Figs. 2 and 3. In Fig. 3, the extremal dimension of the octahedral portion of the electron jack in the direction from Γ to H indicates that an anomaly might occur at a wave vector of approximately 0.76 (reduced units) in the [001] direction. The line BC of Fig. 2 indicates that anomalous behavior might occur at a wave vector of approximately 0.72 (reduced units) in the [111] direction. Also in Fig. 2 the extremal dimension of the Fermi surface in the direction from Γ to N predicts an anomaly at a wave vector of approximately 0.37 (reduced units) in the [011] direction. A careful study of the dispersion relations (Fig. 1) neither substantiates nor refutes the existence of these anomalies.

The recent band-structure calculations of Connolly[14] and Asano and Yamashita[13] also consider the antiferromagnetic state of chromium. Each calculation shows energy gaps which tend to cancel out the electron surface around Γ and the hole surface around H (see Figs. 2 and 3) thus destroying the possibility of any prominent nesting portions of the Fermi surface. However, the relation between the energy gaps and the Fermi surface is dependent upon the Fermi energy, and it is not clear from these calculations whether the Fermi surface of antiferromagnetic chromium will be substantially different from the Fermi surface of paramagnetic chromium. A further investigation of the dispersion relations of chromium above the Néel temperature and well below the Néel temperature might serve to clarify this question.

A calculation of the frequency distribution of chromium is of interest due to recent theoretical and experimental studies of neutron scattering from crystals with substitutional defects.[18-20] A fourth-nearest-neighbor Born–von Kármán analysis was utilized by Feldman[21] to describe the earlier dispersion relations of chromium. The fourth-nearest-neighbor model was appropriate and will be utilized here. A Born–von Kármán analysis is not intended to describe any anomalous behavior in the dispersion relations. Consequently, the data in the regions of anomalous behavior have been ignored in carrying out the theoretical analysis. The solid line in Fig. 1 represents a fourth-nearest-neighbor Born–von Kármán analysis of the present data. The average difference between the theory and experiment is on the order of 3%. The theoretical analysis emphasizes the anomalous depressions in the dispersion relations at the N and H symmetry points (see Figs. 1 and 4). The force constants determined by this analysis are given in Table I.

A histogram representation of the frequency distribution function for chromium has also been calculated. The resulting distribution is shown in Fig. 5. Since the fourth-nearest-neighbor analysis is a good representation of the experimental data,

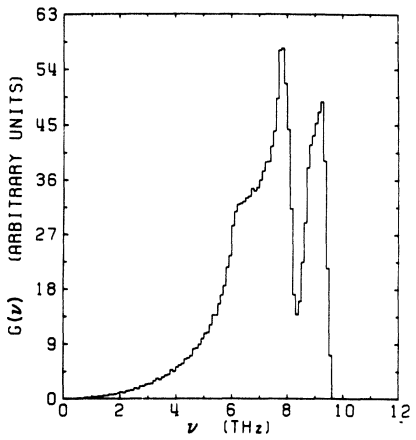

FIG. 5. Histogram representation of the frequency distribution for chromium.

TABLE I. Fourth-nearest-neighbor force constants $\Phi^s_{\alpha,\beta}$ (10^3 dyn/cm).

	1	2	3	4
Φ_{xx}	13.526	35.915	2.042	−1.257
Φ_{yy}	Φ_{xx}	−1.564	Φ_{xx}	0.432
Φ_{zz}	Φ_{xx}	Φ_{yy}	−0.050	Φ_{yy}
Φ_{xy}	6.487	0.0	2.871	0.007
Φ_{xz}	Φ_{xy}	0.0	0.0	Φ_{xy}
Φ_{yz}	Φ_{xy}	0.0	0.0	0.516

the frequency distribution is assumed to be accurate within the ability of the model to calculate frequencies in off-symmetry directions.

CONCLUSION

Four regions of anomalous behavior, not previously observed, have been shown to exist in the phonon dispersion relations of chromium. Those regions which have been shown to arise from the structure of the Fermi surface are identified by arrows in Fig. 1. The anomalous behavior in the phonon dispersion relations of chromium is quite similar to that in molybdenum and, where comparisons are possible, to that of tungsten. This similar anomalous behavior is assumed to be due to the similarity of their Fermi surfaces. Since the data demonstrate that such anomalous behavior can be observed in the phonon dispersion relations of chromium, it is of interest to continue the investigation to determine if these anomalies are substantially different in the paramagnetic and antiferromagnetic states. Further, since alloying small concentrations of manganese or vanadium into chromium slightly changes the band structure, it is of interest to see if the positions of the anomalous behavior might shift with alloying. These experiments have been undertaken and the results will soon be available.

ACKNOWLEDGMENTS

The authors wish to express appreciation to Professor H. R. Danner and Professor W. B. DeFacio for their advice and many helpful discussions.

*Work supported by the National Science Foundation under Grant No. NSF-GP-10773. This paper is based on a thesis submitted by W. M. Shaw in partial fulfillment of the requirements for the Ph. D. degree in Physics at the University of Missouri—Columbia.

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