Phonon Dispersion Relation for Iron*

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The room-temperature phonon dispersion relation of α-Fe has been measured by using the neutron-inelastic-scattering technique. Measurements were taken on phonon groups with their wave vectors in the principal symmetry directions. A Born–von-Kármán fifth-neighbor general-force-constant model was used to analyze the data, and the phonon distribution function was obtained from the force-constant model. We see no evidence for anomalous behavior in the phonon-dispersion curves; on the contrary, the phonon spectrum is remarkably well behaved when compared with the results of the experiments performed on other bcc transition metals (Nb, Ta, Mo, and W).

I. INTRODUCTION

SINCE the pioneering work by Brockhouse and co-workers,[1] the inelastic scattering of thermal neutrons by the phonon excitations in solids has become a powerful technique for studying the lattice dynamics of solids. The conservation of crystal momentum (modulo a reciprocal lattice vector) and the conservation of energy in the coherent scattering of thermal neutrons lead to the dispersion relations for the lattice excitations of the solid.

The unique position of pure iron metal in the itinerant electron theory of the magnetism of metals warrants a comprehensive study of its lattice excitation spectrum. Moreover, since one of the objects of a theory of metals is to calculate the phonon spectrum, one can expect that experimental results for iron will be of use in the development of the theory for those metals in which band admixture is of great importance. At the same time, its high neutron coherent scattering cross section (11.4 b) combined with its low incoherent (0.4 b) and absorption cross sections (1.4 b) allow the collection of reasonable phonon group intensities with comparatively small sample volumes. For these reasons, then, iron becomes a natural candidate for an inelastic neutron-scattering experiment. The first attempt to measure the phonon spectrum of iron was carried out by Low[2] using the time-of-flight technique. While in the process of analyzing our data, we became aware of measurements carried out independently by Brockhouse *et al.*[3] and Bergsma *et al.*[4] with a three-crystal spectrometer. A comparison will be made with the results of two more recent experiments. In the present experiment, phonon groups were measured with their wave vectors along the $[0,0,\zeta]$, $[\zeta,\zeta,0]$, $[\zeta,\zeta,\zeta]$, $[\zeta,\zeta,1]$, and the $[\frac{1}{2},\frac{1}{2},\zeta]$ symmetry directions.

In recent years, the pseudopotential theory of metals[5–9] has provided an elegant theoretical framework within which one can describe the properties of the simple metals. However, the approximations that have been used in the pseudopotential formalism, in particular the small-core approximation, preclude the possibility of using the theory to calculate the properties of the more complicated metals. Thus for want of a more appropriate theory for these metals, their phonon spectra have normally been analyzed along the lines of the Born–von-Kármán theory of lattice vibrations, with the hope that it would provide a convenient method of collecting and comparing the results of measurements on different systems. Woods,[10] for example, has analyzed the phonon spectra of the bcc transition metals niobium, tantalum, molybdenum, and tungsten and has shown that a pattern does indeed exist for the force constants of these metals.

In practice, the Born–von-Kármán theory consists of assigning a force-constant matrix to each of the neighbors of a particular atom, constructing the dynamical matrix from the individual force-constant matrices, and then solving the dynamical matrix for the phonon energies and the associated phonon polarizations. For example, in the bcc lattice with one atom in the unit cell, the atom at the $\frac{1}{2}a(1,1,1)$ position is given a force-constant matrix of the form

$$\begin{pmatrix} \alpha_1 & \beta_1 & \beta_1 \\ \beta_1 & \alpha_1 & \beta_1 \\ \beta_1 & \beta_1 & \alpha_1 \end{pmatrix} \tag{1}$$

where the elements of the matrix can be interpreted as the force on the atom at the origin in the ith direction when the first neighbor atom is given a unit displacement along the jth direction. The force constants are substituted into the equations of motion

$$m\ddot{\epsilon}_i = \sum_j \sum_l \varphi_{ij}(l)\epsilon_j \tag{2}$$

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[3] B. N. Brockhouse, H. Abou-Helal, and E. D. Hallman, Solid State Commun. **5**, 211 (1967).

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[9] W. A. Harrison, in *The Frontiers in Physics*, edited by D. Pines (W. A. Benjamin, Inc. New York, 1966).

[10] A. D. B. Woods, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1964), Vol. I, p. 87.

TABLE I. Experimental values of the phonon energy E for the $[q,q,0]$ and $[q,q,q]$ directions.

q(Å^{-1})	E(meV)	q(Å^{-1})	E(meV)	q(Å^{-1})	E(meV)	q(Å^{-1})	E(meV)
$L[q,q,0]$		$T_2[q,q,0]$		$L[q,q,q]$		$T[q,q,q]$	
0.141	7.5±0.3	0.219	7.9±0.2	0.231	15.5±0.4	0.231	7.9±0.4
0.212	11.5±0.3	0.329	11.9±0.2	0.346	22.4±0.5	0.346	12.0±0.2
0.230	12.9±0.2	0.438	15.4±0.2	0.462	28.0±0.5	0.462	16.1±0.2
0.248	13.8±0.2	0.548	18.5±0.2	0.577	32.7±0.5	0.577	19.9±0.3
0.265	14.8±0.2	0.566	19.0±0.2	0.693	33.9±0.4	0.693	23.4±0.4
0.283	15.6±0.3	0.636	20.8±0.2	0.751	34.7±0.4	0.808	25.8±0.2
0.301	16.6±0.2	0.707	22.4±0.2	0.808	34.6±0.3	0.924	27.8±0.2
0.318	17.4±0.2	0.778	23.9±0.2	0.924	33.8±0.2	1.039	29.4±0.2
0.336	18.3±0.2	0.849	25.1±0.2	1.039	31.4±0.3	1.155	30.4±0.2
0.354	18.9±0.3	0.919	26.1±0.2	1.097	29.8±0.2	1.270	31.8±0.2
0.424	22.3±0.3	0.990	26.5±0.2	1.155	28.5±0.1	1.386	32.9±0.3
0.495	25.5±0.3	1.061	26.7±0.2	1.212	27.3±0.1	1.501	33.4±0.3
0.566	28.6±0.2	1.096	26.7±0.2	1.270	25.9±0.1	1.617	34.5±0.3
0.636	31.3±0.2			1.328	24.7±0.2	1.732	34.4±0.4
0.707	33.6±0.2			1.386	23.8±0.1	1.848	34.9±0.6
0.743	34.4±0.3	$T_1[q,q,0]$		1.501	23.7±0.4	1.963	35.1±0.4
0.778	35.5±0.3	1.096	18.5±0.3	1.617	24.9±0.5	2.079	35.6±0.4
0.813	36.1±0.3			1.730	27.7±0.2	2.192	35.4±0.2
0.884	37.1±0.3			1.846	30.4±0.2		
0.955	38.2±0.3			1.961	33.2±0.2		
1.025	38.3±0.4			2.077	34.9±0.3		
1.096	38.3±0.5			2.192	35.4±0.2		

and the equations of motion are then solved for the phonon energies as a function of α_1 and β_1; in Eq. (2), m is the mass of the vibrating atom, the $\varphi_{ij}(l)$ are the elements of the force-constant matrix for the lth neighbor, and ϵ_i is the displacement of the atom along the ith direction from its equilibrium position. The elements α_1 and β_1 can then be used as the first-neighbor parameters in a least-squares fit to the data. In addition, one can restrict the analysis to force systems that are of the central or the axially symmetric type; this amounts to introducing relationships among the elements of the force-constant matrices, so that not all of the elements are independent parameters in the fit to the data. The force constants can also be of great value as a simple mathematical description of the phonon spectrum. Gilat and Raubenheimer[11] have used this property in their method of calculating the phonon distribution function. Once the distribution function is known, one can calculate the thermodynamic properties (specific heat, Debye temperature, etc.) of the lattice within the harmonic approximation. This approach was used in the present study, and the results are presented in the next section.

II. EXPERIMENTAL METHOD AND RESULTS

All the data were collected at the Brookhaven high flux beam reactor using a standard three-crystal spectrometer to analyze the outgoing neutron energy and momentum. Incoming neutron energies of 45 and 65 meV were used to collect the majority of the data points with the spectrometer operated in the constant-Q mode and the incident neutron momentum fixed. To limit the energy and momentum spread of the beam, collimations of 30 and 20 min were normally used, before and after the scattering. The sample was an excellent cylindrical single crystal with the dimensions $1\frac{1}{2}$ in. in height and $\frac{1}{2}$ in. in diam. The mosaic spread of the crystal, measured with a perfect germanium crystal as a monochromator, was 7 min. full width at half-maximum. The crystal was grown by the strain-anneal method by Monocrystal Company of Cleveland, Ohio.

An attempt was made to make a rather complete study of the phonon-dispersion surface and toward this end a total of 126 phonon groups were measured and analyzed. The data are given in Tables I and II and plotted in Figs. 1–3. Two examples of the experimental phonon group profiles are given in Fig. 4. The accuracy of the experiment performed by Brockhouse *et al*[3]. is comparable to ours (~1%), although the number of phonon modes they measured is approximately $\frac{1}{3}$ of those measured in the present experiment. As is shown by Brockhouse *et al.*,[3] the agreement between the two sets of data is quite satisfactory. However, a comparison with the results of Bergsma *et al.*[4] shows a rather serious

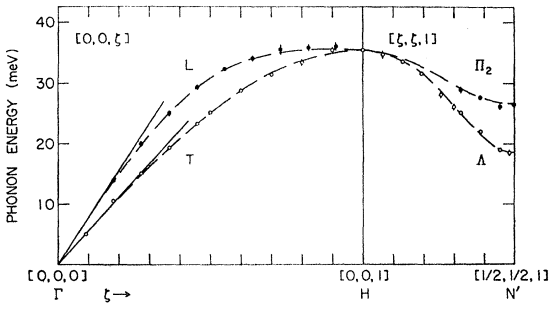

FIG. 1. The room-temperature phonon dispersion curves of α-Fe along the [0,0,ζ] and [ζ,ζ,1] directions.

[11] G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).

TABLE II. Experimental values of the phonon energy E for the $[0,0,q]$, $[\pi/a,\pi/a,q]$, and $[q,q,2\pi/a]$ directions.

q(Å^{-1})	E(meV)	q(Å^{-1})	E(meV)
$L[0,0,q]$		$T[0,0,q]$	
0.4	13.8±0.3	0.2	5.0±0.2
0.6	19.8±0.4	0.4	10.2±0.05
0.8	25.0±0.4	0.6	15.0±0.1
1.0	29.3±0.4	0.8	19.3±0.2
1.2	32.2±0.3	1.0	23.3±0.2
1.4	34.2±0.4	1.096	25.1±0.2
1.6	35.5±0.7	1.315	28.7±0.2
1.8	35.8±0.5	1.534	31.4±0.3
2.0	36.0±0.6	1.753	33.4±0.5
2.192	35.4±0.2	1.973	35.4±0.5
		2.192	35.4±0.2
$\pi[\pi/a,\pi/a,q]$		$\Lambda[\pi/a,\pi/a,q]$	
0.2	38.3±0.4	1.292	29.4±0.4
0.3	37.3±0.5	1.492	28.8±0.5
0.4	36.8±0.4	1.692	28.0±0.3
0.6	35.4±0.3	1.892	27.4±0.4
0.8	33.3±0.3	2.092	26.7±0.4
1.0	31.0±0.3		
1.2	28.8±0.3		
1.492	25.7±0.4		
1.692	22.4±0.5		
1.892	20.1±0.3		
2.092	18.8±0.2		
$\Lambda[q,q,2\pi/a]$		$\pi_2[q,q,2\pi/a]$	
0.141	34.9±0.5	0.707	28.9±0.5
0.283	33.6±0.4	0.849	27.7±0.4
0.424	31.6±0.3	0.990	26.2±0.4
0.566	28.1±0.5	1.096	26.7±0.2
0.658	26.1±0.5		
0.707	25.2±0.3		
0.849	22.1±0.3		
0.990	19.1±0.3		
1.061	18.5±0.5		

disagreement for the longitudinal modes with their wave vectors near the zone boundary in the $[\zeta,\zeta,0]$ direction. For example, our value for the zone-boundary energy in the $[\zeta,\zeta,0]$ direction is approximately 5% lower than that quoted by Bergsma *et al.*[4]; the difference is well outside of our experimental error. No attempts were made to extract the phonon lifetimes from the widths of the inelastic neutron groups; in fact, the analysis of Cooper and Nathans[12] showed that an overwhelming fraction of the observed widths for a number of representative phonon groups could be attributed to the instrumental resolution function.

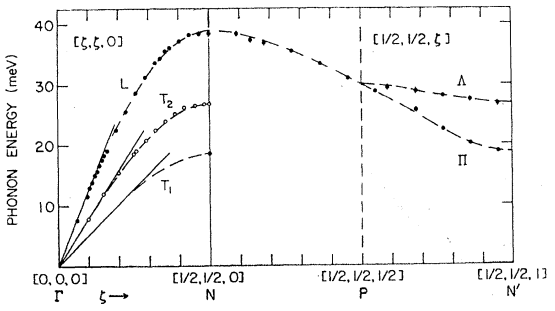

FIG. 2. The room-temperature phonon dispersion curves of α-Fe along the $[\zeta,\zeta,0]$ and $[\frac{1}{2},\frac{1}{2},\zeta]$.

[12] M. J. Cooper and R. Nathans (to be published).

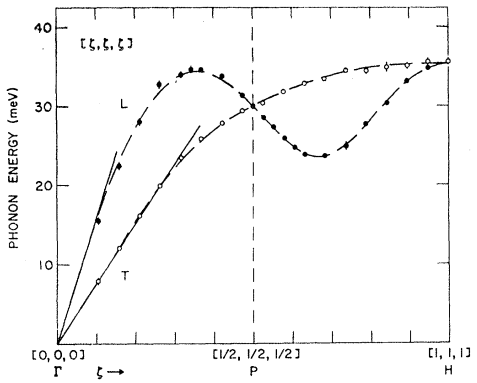

FIG. 3. The room-temperature phonon dispersion curves of α-Fe along the $[\zeta,\zeta,\zeta]$ direction.

As noted before, we have analyzed the data along the lines of the Born–von-Kármán theory of lattice vibrations. A number of models were used in a linear least-squares fit to the data. We found that the axially symmetric force models did not seem to fit the data quite as well as the tensor models, and that in any case, we had to include interactions out to at least the third-neighbor atoms. The dashed curves on Figs. 1–3 are the result of the least-squares fit of the data to a fifth-neighbor tensor model; the elements of the force-constant matrices are given in Table III. The solid straight lines in Figs. 1–3 are the appropriate sound velocities as calculated from the elastic constants of Rayne and Chandrasekhar.[13]

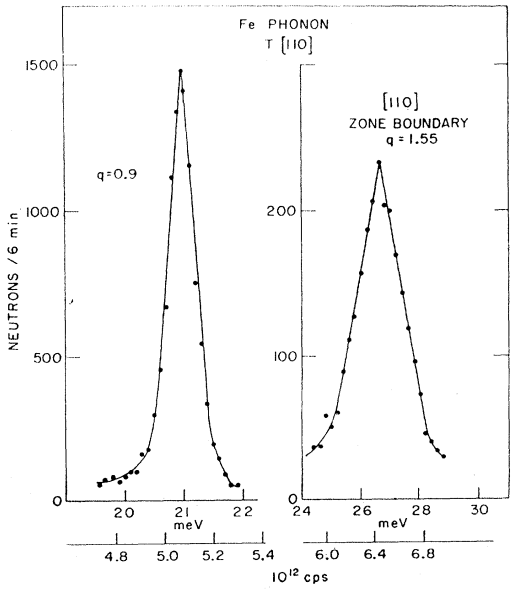

FIG. 4. Examples of phonon group profiles in the $[q/\sqrt{2},q/\sqrt{2},0]$ symmetry direction.

[13] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **122**, 1714 (1961).

TABLE III. The elements of the force-constant matrices (in units of 10^4 dyn/cm) from a least-squares fit of the data to a fifth-neighbor general-force-constant model. The notation is taken from Woods.[a]

Atom position				
$\frac{1}{2}a(1,1,1)$	$\frac{1}{2}a(2,0,0)$	$\frac{1}{2}a(2,2,0)$	$\frac{1}{2}a(3,1,1)$	$\frac{1}{2}a(2,2,2)$
$\alpha_1(XX)$ 1.688	$\alpha_2(XX)$ 1.463	$\alpha_3(XX)$ 0.092	$\alpha_4(XX)$ −0.012	$\alpha_5(XX)$ −0.029
$\beta_1(XY)$ 1.501	$\beta_2(YY)$ 0.055	$\beta_3(YY)$ −0.057	$\beta_4(YY)$ 0.003	$\beta_5(XY)$ +0.032
		$\gamma_3(XY)$ 0.069	$\gamma_4(XZ)$ 0.052	
			$\delta_4(XY)$ 0.0007	

[a] A. D. B. Woods, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 3.

The force constants that we obtained for the fifth-neighbor tensor model were compared with those obtained by Brockhouse *et al.*[3]; the agreement is quite reasonable, and , in particular, we agree with the result that α_1 is larger than β_1, which is an inequality peculiar[3] to the bcc transition metals that have been studied to date.

The phonon frequency distribution function $g(\nu)$ has been calculated by the method of Gilat and Raubenheimer,[12] and is given in Fig. 5. The channel width, which corresponds to the resolution in frequency space with which one wants to define the distribution function, that has been used in the calculation for $g(\nu)$, is 1.5×10^9 cps. It should be noted that inherent in the calculation for $g(\nu)$ is the assumption that the force constants obtained from the phonon spectra along the symmetry directions can be used to calculate the phonon frequencies throughout the entire zone. This assumption is justified in our case, since we see no evidence for a sharp break or Kohn anomaly along the principal symmetry directions in the phonon spectrum of this metal. Gilat[14] has recently shown that the distribution function of this metal has a rather unique singularly at 8.58×10^{22} cps; the singularity is one for which the amplitude of $g(\nu)$ is logarithmically divergent, the divergence being probably limited by anharmonic effects.

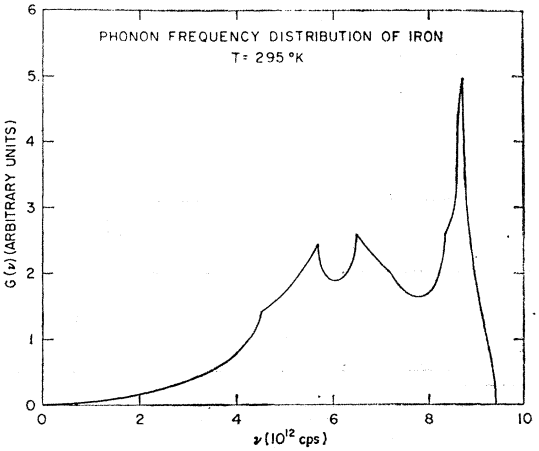

FIG. 5. The phonon distribution function of α-Fe calculated from the fifth-neighbor general-force-constant model.

III. DISCUSSION

To satisfactorily reproduce the phonon spectrum of α-Fe, we have used a Born–von-Kármán force-constant model that includes interactions out to the fifth-neighbor atoms; the fact that the force system includes interactions out to the distant atoms is indicative, to some extent, of the metallic nature of the interatomic forces. One might have hoped that the phonon spectrum would reflect some of the properties of the band structure of the metal in a fairly straightforward way, but the results of the experiment have shown that the excitation spectrum has the rather normal behavior. The spectrum is far from being as complicated as the spectra taken for some of the other bcc transition metals. In fact, the phonon distribution functions of α-Fe and the simple metal potassium are, at least qualitatively, very similar.

An attempt was made to analyze the data with a model for iron that was physically more appealing. We tried to separate, in some sense, the total interatomic interaction into a nearest-neighbor bonding or "quasi-bonding" contribution and a metallic contribution. The Born–von-Kármán approach was used to parametrize the bonding nearest-neighbor interaction, while a reciprocal-space analysis, similar to the analysis used recently by Cowley *et al.*[15] for potassium, was used to characterize the metallic contribution to the total interatomic interaction. The dynamical matrix was constructed and the parameters in the dynamical matrix were used as the variables in a nonlinear least-squares fit to the data. We could not obtain satisfactory results; we are, however, continuing our effort in this direction.

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[14] G. Gilat, Phys. Rev. **157**, 540 (1967).
[15] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev **150**, 487 (1966).