is 545°K), we obtain, for the sample of Ref. 8, the value $\epsilon_f=0.87$ eV. If we make the approximation that the jump frequency ω_j is given by

$$\omega_j\approx\omega_D \exp(-\epsilon_+/kT), \tag{78}$$

where $\omega_D\approx120$°K is the Debye frequency of bismuth, and if we assume a jump frequency of one cps at $T=\frac{1}{2}$ the melting point, we obtain the value $\epsilon_+=0.68$ eV.

The above analysis corresponds to the following physical situation: The defects are frozen in the solid at a temperature not far below room temperature. The energy of formation is somewhat lower than that usually found in solids, corresponding to the somewhat loose packing of the atoms in bismuth. The activation energy is lower than the energy of formation, which is always the case in a solid.

VI. CONCLUDING REMARKS

We conclude that serious consideration must be given to the possibility of Frenkel defects being the dominant scattering centers in very pure, well-annealed bismuth single crystals at cryogenic temperatures. This possibility suggests the desirability of carrying out galvanomagnetic studies, including Alfvén-wave experiments, on irradiated and/or quenched bismuth single crystals.

ACKNOWLEDGMENTS

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Phonon Frequencies in Copper at 49 and 298°K*

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Phonon frequencies for wave vectors along the principal symmetry directions in copper have been determined at 49 and 298°K from neutron inelastic-scattering measurements. In general, the temperature dependences of the frequencies were found to be smaller for the higher-frequency modes. For the lower frequencies ($\nu\lesssim3\times10^{12}$ cps), the frequency changes measured are consistent with the 3–4% changes estimated from the isothermal elastic constants. For higher frequencies the relative changes are much smaller, often being 1% or less. Axially symmetric force models, which included interactions to the sixth nearest neighbors, were fitted to the data and have been used to calculate a frequency distribution function $g(\nu)$ at each temperature. A comparison of the temperature dependences of the moments of these distributions with various Grüneisen parameters leads to the conclusion that Cu does not satisfy the assumption of the quasi-harmonic model. The Debye temperature Θ_C versus temperature curve calculated with the 49°K $g(\nu)$ is in excellent agreement with results from specific-heat measurements in the entire 0 to 298°K range. A fairly strong temperature dependence for the widths of some well-focused phonons was observed.

INTRODUCTION

MEASUREMENTS of the coherent inelastic scattering of neutrons by solids can give directly the phonon dispersion relations $\nu(q)$ and, in principle, considerable information about interatomic forces.[1] However, the analyses of such measurements are always made on the basis of a harmonic theory, whereas the measurements are usually obtained under conditions in which anharmonic effects are not negligible. Although one expects a harmonic analysis of the data to yield qualitatively correct conclusions, the development of a truly quantitative description of the interatomic forces requires a better understanding of anharmonicity. Even the most accurate interpolation formula for the dispersion relations will yield a frequency distribution function $g(\nu)$ of dubious value, because anharmonicity affects differently the various physical properties that, in a harmonic theory, depend on $g(\nu)$.[2] To take a proper account of anharmonicity in a force model analysis of dispersion curve data is prohibitively complex, however, judging from the theoretical work in the literature.[3–5] Thus, at the present time it seems that a more fruitful examination of anharmonicity involves the measurement of the temperature (and pressure) dependences of the energies and lifetimes of phonons as well as the

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[1] See for example, G. Dolling and A. D. B. Woods, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chap. 5.

[2] T. H. K. Barron, in *Proceedings of the International Conference on Lattice Dynamics at Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1963), p. 247.
[3] A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).
[4] R. A. Cowley, Advan. Phys. **12**, 421 (1963).
[5] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) **287**, 259 (1965).

correlation of such measurements with other physical properties affected by anharmonicity.

In the present paper, we report principally measurements of the phonon frequencies in Cu at 49°K for wave vectors along the principal symmetry directions. The results were determined from measurements of the coherent inelastic scattering of thermal neutrons, obtained on a triple-axis neutron spectrometer. A fairly extensive study of the phonon frequencies in Cu at 298°K was also made in order that conclusions about the temperature dependences of these frequencies could be based on the comparison of data obtained under identical experimental conditions. The analyses of our 298°K data are not discussed in detail, because the data are in good agreement with those reported in two recent neutron scattering studies of the lattice dynamics of Cu at room temperature.[6,7] However, a critical comparison of our work with these other studies has been made and is discussed briefly.

The comparison of the low-temperature data with our own room temperature measurements is made primarily by means of calculations based on Born–von Kármán interatomic force models that were fit to both sets of data. These calculations also provide a basis for the comparison of these neutron scattering results with a variety of thermodynamic properties of Cu. The changes in the frequencies and widths of a few well-focused phonon peaks are also discussed.

MEASUREMENTS AND RESULTS

A schematic illustration of the neutron spectrometer used to obtain the data is shown in Fig. 1. The spectrometer is, of course, similar in principle to those described elsewhere.[8] The monochromator crystal (M_1 in Fig. 1), bathed in a neutron beam from the reactor, diffracts neutrons with mean energy E_0 and momentum $\hbar\mathbf{k}_0$ toward the sample S. The neutrons scattered by the sample with energy E' and momentum $\hbar\mathbf{k}'$ are then diffracted by the analyzer crystal A into the BF_3 detector. One-phonon coherent scattering by the sample occurs when

$$E_0-E'=\pm h\nu(\mathbf{q}),$$

and

$$\mathbf{k}_0-\mathbf{k}'=\mathbf{Q}=2\pi\boldsymbol{\tau}+\mathbf{q}, \qquad (1)$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector, $\mathbf{q}$ is the phonon wave vector, $\nu(\mathbf{q})$ is the phonon frequency, and the $+(-)$ sign corresponds to energy loss (gain) processes related to phonon creation (annihilation).

The majority of the data was obtained with the "constant-Q" method, although at 298°K some data were obtained with the "constant-E" method.[9] In this

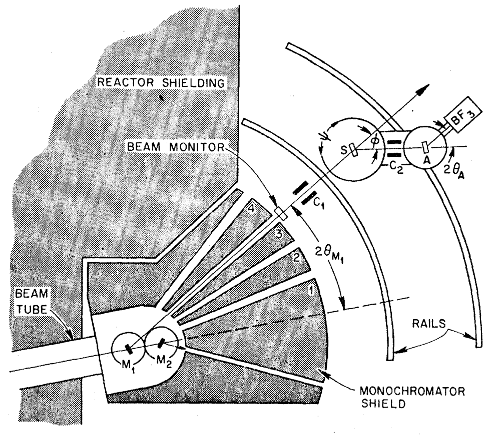

FIG. 1. Schematic diagram of the triple-axis neutron spectrometer at the Oak Ridge Research Reactor.

spectrometer the monochromator diffraction angle $2\theta_{M_1}$ is restricted to the values 11°, 22°, 34°, and 45° which correspond to the beam ports labeled 1, 2, 3, and 4, respectively, in Fig. 1. Thus the constant-Q experiments were done with E' varied and with E_0 fixed at either 80.4 meV for study of the higher-frequency phonons or at 46.9 meV for study of the lower-frequency phonons. These values for E_0 were obtained with the $(10\bar{1}1)$ Bragg reflection of a Be monochromator and beam ports 3 and 4, respectively. The neutron flux at the sample was typically $\sim 0.5\times 10^7 n/\mathrm{cm}^2$ sec. The second axis of the spectrometer can be accurately aligned in the monochromatic beam by the movement of a dolly, on which the sample table is mounted, on the rails shown in Fig. 1. The (0002) Bragg reflection from a second Be crystal was used as an analyzer. The positions of the spectrometer axes (in multiples of 0.01°) are automatically controlled by a paper tape prepared on a computer. Slo-Syn stepping motors and preset indexers are used to drive the various spectrometer shafts. The collimators C_1 and C_2 were either 0.6° or 0.3° (full width at half maximum) Soller slits.

Two cylindrical samples that were approximately 1 in. in diameter and $1\frac{1}{2}$ in. long were studied. One crystal had a [110] crystallographic direction along its axis; the other, a [100] direction. Both crystals were 99.999% pure and had mosaic spreads of $\lesssim 30$ sec.[10]

The low-temperature data were obtained with the samples mounted in a cryostat and the 49°K (±2°) sample temperature was obtained by pumping on solid nitrogen. Some room-temperature data were repeated with each sample mounted in the cryostat in order to verify that systematic errors in the data due to possible changes in the sample alignment and position in the neutron beam were negligible.

[6] S. K. Sinha, Phys. Rev. **143**, 422 (1966).

[7] E. C. Svennson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967).

[8] P. K. Iyengar, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chap. 3.

[9] B. N. Brockhouse, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.

[10] M. C. Wittels, F. A. Sherrill, and F. W. Young, Jr., Appl. Phys. Letters **1**, 22 (1962); **2**, 127 (1963); Phys. Letters **5**, 183 (1963).

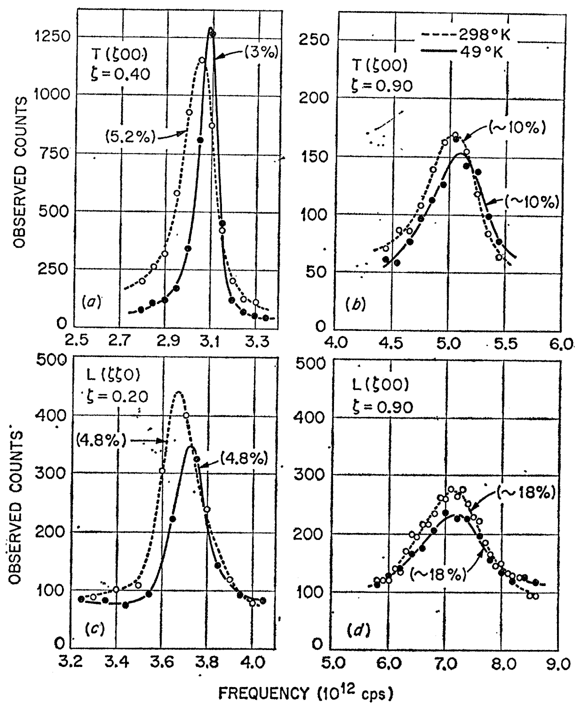

FIG. 2. Several typical phonon peaks for copper obtained in constant-Q experiments.

Examples of several phonon peaks obtained in this study are shown in Fig. 2. The numbers in parentheses are the peak widths at half-maximum, expressed as a percentage of the phonon frequency. The width observed for a phonon peak is largely of instrumental origin and is due to the distribution of energies and momenta in the incident and scattered neutron beams that result from imperfect collimation and the mosaic spreads of the monochromator and analyzer crystals. However, a correlation exists between the energy and momentum distributions that can result in a narrow focused phonon peak.[11] Focusing is strongly dependent on the dispersion curve slope as evidenced by Figs. 2(a) and 2(b). The advantages of examining well-focused peaks in a study of the temperature dependence of phonon frequencies and widths are obvious. Small frequency changes are then relatively easily detected, as illustrated for the peaks in Figs. 2(a) and 2(c). The broader peaks in Figs. 2(b) and 2(d) are typical for phonons measured near zone boundaries and other regions where the dispersion-curve slope is very small or zero. The frequency changes for these phonons are correspondingly much more difficult to measure and consequently have large uncertainties. The majority of the observed phonon peaks had widths between the extremes shown in Fig. 2.

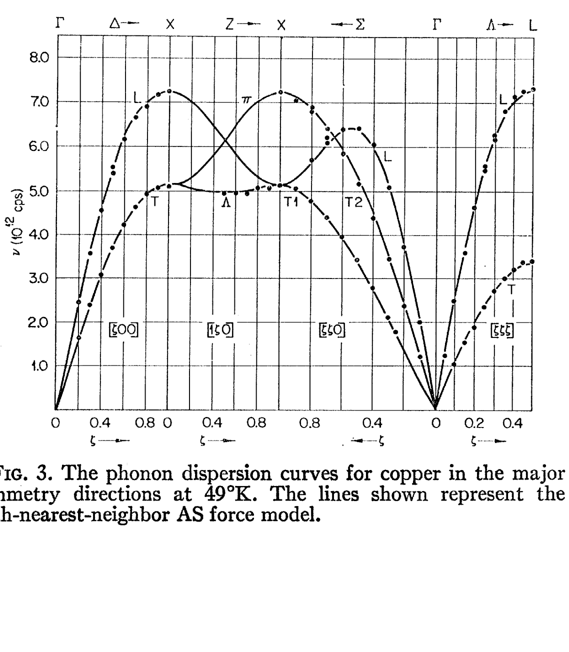

FIG. 3. The phonon dispersion curves for copper in the major symmetry directions at 49°K. The lines shown represent the sixth-nearest-neighbor AS force model.

Several observations about the temperature dependences of the widths of some well-focused phonon peaks are noteworthy. For example, the frequency of the phonon peak shown in Fig. 2(a) changed only ~1% between 49 and 298°K; however, its width increased ~75%. Considering that a large fraction of the width of this peak is probably instrumental, the observed change in width seems very large if due to anharmonic effects, in view of the relatively low sample temperatures compared to the melting temperature (1083°C). In addition, although the observed peak widths for some $T2(\zeta\zeta 0)$ phonons were also in the 3% range at 49°K, their widths changed significantly less, i.e., 30–50%. The width of the $L(\zeta\zeta 0)$ peak shown in Fig. 2(c) has not changed at all, although it is as narrow as some $T(\zeta 00)$ and $T2(\zeta\zeta 0)$ peaks for which significant width changes were measured. Of course, for very narrow peaks the observed width is an extremely sensitive function of the dispersion-curve slope. For the peak in Fig. 2(a), a qualitative computation indicated that a 1% change in slope could change the width 5%. A careful analysis of this effect would be needed before the contribution to the width changes by anharmonic (lifetime) interactions could be determined with confidence.

The 49°K results are summarized in Fig. 3 and in Table I where the frequency changes measured between 49 and 298°K are also listed. At 298°K approximately 250 usable phonon peaks were measured, and many of these corresponded to values of wave vectors not included in Table I. In order to check the consistency of the data, equivalent phonons were measured in two different samples and for different E_0, E', and $\boldsymbol{\tau}$ in Eq. (1). Essentially all such equivalent data agreed within the errors listed in Table I, i.e., usually within 1 to 2%. No corrections have been applied to the data. Estimates of systematic errors in the measured phonon frequencies due to the variation (during a phonon scan) of the analyzer reflectivity and the one-phonon scattering cross section were completely negligible compared to the errors listed in Table I.

[11] M. F. Collins, Brit. J. Appl. Phys. 14, 805 (1963); see also R. Stedman and G. Nilsson, Phys. Rev. 145, 492 (1966).

TABLE I. Normal mode frequencies for the symmetry branches in copper at 49°K and the frequency changes $\Delta\nu=\nu(49°\text{K})-\nu(298°\text{K})$. Frequency units are 10^{12} cps.

ζ	$L(00\zeta)$ ν	$\Delta\nu$	ζ	$T(00\zeta)$ ν	$\Delta\nu$	ζ	$L(\zeta\zeta0)$ ν	$\Delta\nu$
0.20	2.43±0.04	−0.01	0.20	1.65±0.02	0.05	0.10	2.01±0.02	0.05
0.30	3.56±0.04	0.00	0.30	2.40±0.02	0.05	0.20	3.73±0.03	0.06
0.40	4.56±0.05	0.06	0.40	3.09±0.02	0.04	0.30	5.10±0.07	0.07
0.50	5.44±0.07	0.02	0.50	3.69±0.03	0.02	0.40	6.05±0.10	0.05
0.60	6.15±0.10	0.01	0.60	4.22±0.03	0.05	0.50	6.42±0.15	0.07
0.70	6.66±0.10	0.00	0.70	4.64±0.05	0.05	0.60	6.39±0.15	0.04
0.80	6.90±0.15	0.00	0.80	4.94±0.10	0.06	0.70	6.18±0.10	0.04
0.90	7.18±0.17	0.03	0.90	5.08±0.10	0.01	0.80	5.80±0.15	0.09
1.00	7.25±0.20	0.05	1.00	5.13±0.15	0.04	1.00	5.13±0.15	0.04
	$T1(\zeta\zeta0)$[a]			$T2(\zeta\zeta0)$[a]				
0.25	1.79±0.03	0.06	0.10	1.21±0.015	0.09			
0.30	2.12±0.04	(0.05)[b]	0.20	2.385±0.020	0.04			
0.40	2.79±0.03	(0.06)[b]	0.30	3.46±0.03	0.05			
0.50	3.43±0.04	(0.04)[b]	0.40	4.39±0.03	0.06			
0.60	3.93±0.07	0.08	0.50	5.16±0.06	0.04			
0.70	4.40±0.05	0.07	0.60	5.85±0.07	0.09			
0.80	4.80±0.06	0.10	0.70	6.40±0.12	0.01			
0.90	5.07±0.10	0.14	0.80	6.84±0.15	0.05			
1.00	5.13±0.15	0.04	0.90	7.05±0.20	−0.03			
			1.00	7.25±0.20	0.05			
	$L(\zeta\zeta\zeta)$			$T(\zeta\zeta\zeta)$			$\Lambda(10\zeta)$	
0.05	1.22±0.03	...	0.10	1.05±0.06	0.07	0.50	4.95±0.09	0.06
0.10	2.49±0.05	...	0.15	1.53±0.06	(0.09)[b]	0.60	4.96±0.09	−0.01
0.15	3.59±0.05	...	0.20	1.90±0.06	(0.01)	0.70	4.98±0.10	−0.02
0.20	4.61±0.05	0.04	0.25	2.35±0.04	(0.05)	0.80	5.08±0.10	0.06
0.25	5.51±0.10	0.05	0.30	2.72±0.05	(0.03)	0.90	5.11±0.10	0.06
0.30	6.21±0.10	0.03	0.35	3.03±0.06	(0.05)	1.00	5.13±0.15	0.04
0.35	6.80±0.15	0.09	0.40	3.24±0.07	(0.03)			
0.40	7.12±0.15	0.11	0.45	3.39±0.08	(0.02)			
0.45	7.27±0.20	0.11	0.50	3.42±0.10	0.01			
0.50	7.30±0.20	0.01						

[a] The polarization vectors for the $T1$ and $T2(\zeta\zeta0)$ branches are parallel to $[\bar{\zeta}\zeta0]$ and $[00\zeta]$, respectively.
[b] Phonons were not measured exactly at these ζ values at 298°K. The frequency changes shown were obtained by interpolation.

The small dependences on temperature of the phonon frequencies in Cu are noteworthy. At small values of ζ (0.1–0.2), the measured frequency changes are generally consistent with the 3–4% changes estimated for the very low-frequency modes from isothermal elastic constants.[12] However, at higher ζ values the changes are only 1–2% or less. Because of the small changes that were found, the data were carefully checked, and a number of phonons were remeasured to establish a confidence in the results. Thus, although the frequency change for a given phonon is often within the estimated experimental errors, the combined results for a large number of measurements definitely show that the effect is real.

The agreement of our room-temperature data with previous work[6,7] is quite satisfactory. All the data of Sinha[6] correspond to "off-symmetry" phonon wave vectors, but the frequencies corresponding to symmetry directions that were obtained from extrapolation are in agreement with our data, where overlap exists, within the combined experimental errors. The errors reported by Sinha are about a factor of 2–3 larger than those obtained in these measurements. The over-all agreement of our data with those of Svennson *et al.*[7] is somewhat better. Although the disagreement is generally systematic (our data often yield slightly higher frequencies) and for several $L(\zeta\zeta0)$ phonons near $\zeta=0.75$ it is as high as 4%, the over-all agreement is about 1%. This agreement is better than the average experimental error of about 2% for each set of data and lends some support to the contention of Svensson and his associates that errors conventionally assigned to the frequencies obtained in neutron-scattering experiments are too large by a factor of 2.

[12] W. C. Overton, Jr., and John Gaffney, Phys. Rev. 98, 969 (1955).

FORCE MODELS AND THERMODYNAMIC CALCULATIONS

Both the 49 and 298°K data were fit by several different types of Born–von Kármán atomic force models. Models in which the forces were assumed to be all general, all axially symmetric (AS), or a mixture of general and axially symmetric were examined. A general force model cannot be extended beyond the fourth-nearest neighbor if the interaction parameters (force constants) are to be determined from an analysis of high symmetry data alone. And although a general fourth-neighbor force model (12 parameters) gave a fairly good fit to our data, a significantly better fit was obtained with a sixth-nearest-neighbor AS model (also 12 parameters). The fit to the data was not improved

TABLE II. Best fit sixth-nearest-neighbor axially symmetric models.

Neighbor and location		Force constants (dyn/cm) 49°K	298°K	Restrictions for the axially symmetric model
1(110)	α_1^1	13278	13124	
	α_3^1	−1351	−1503	
	β_3^1	14629	14626	$\beta_3^1=\alpha_1^1-\alpha_3^1$
2(200)	α_1^2	−41	525	
	α_2^2	−198	−265	
3(211)	α_1^3	742	867	
	α_2^3	284	379	
	β_1^3	153	163	$\beta_1^3=\frac{1}{3}(\alpha_1^3-\alpha_2^3)$
	β_2^3	306	325	$\beta_2^3=\frac{2}{3}(\alpha_1^3-\alpha_2^3)$
4(220)	α_1^4	350	237	
	α_3^4	−327	−372	
	β_3^4	677	609	$\beta_3^4=\alpha_1^4-\alpha_3^4$
5(310)	α_1^5	−195	−352	
	α_2^5	−6	−51	
	α_3^5	17	−14	$\alpha_3^5=\frac{1}{8}(9\alpha_2^5-\alpha_1^5)$
	β_3^5	−71	−113	$\beta_3^5=\frac{3}{8}(\alpha_1^5-\alpha_2^5)$
6(222)	α_1^6	−137	−159	
	β_1^6	−135	−213	

Force constant matrix: $\begin{pmatrix}\alpha_1^n & \beta_3^n & \beta_2^n\\ \beta_3^n & \alpha_2^n & \beta_1^n\\ \beta_2^n & \beta_1^n & \alpha_3^n\end{pmatrix}$

by extending the AS model to further than six nearest neighbors, nor by adding one additional parameter to allow for a general (tensor) first-nearest-neighbor interaction. In all the fitting attempts, the isothermal elastic constants measured at each temperature[12] were used as independent data. Generally, the models which gave a good fit to the neutron data also yielded elastic constants in good agreement with experiment. The fit to the 49°K data obtained with the sixth-neighbor AS model is illustrated in Fig. 3. The force constants of this model are compared to those obtained by fitting the same type of model to our 298°K data in Table II.

From the sixth-neighbor AS models in Table II, we have computed a frequency distribution function $g(\nu)$, for both 49 and 298°K, using the method recently developed by Gilat and Raubenheimer.[13] These distributions are shown in Fig. 4. There is very little difference in these two distributions as one would expect on the basis of the very small changes in the measured phonon frequencies. There is essentially no change in the cutoff frequencies of these distributions.

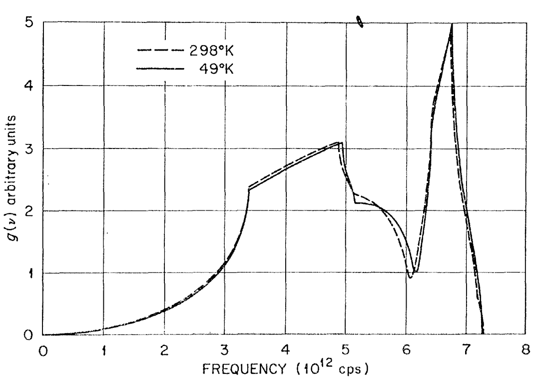

FIG. 4. Frequency distributions at 49 and 298°K for copper.

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

An alternative means of comparing these distributions involves the moments

$$\mu_n=\int_0^\infty \nu^n g(\nu)d\nu \bigg/ \int_0^\infty g(\nu)d\nu \tag{2}$$

or the Debye "cutoff" frequencies[14]

$$\nu_n=\left[\frac{n+3}{3}\mu_n\right]^{1/n}; \quad n\neq 0,\ n>-3, \tag{3}$$

$$\nu_{-3}=(h/k_B)\Theta_C(0°), \tag{4}$$

$$\nu_0=\exp\left[\frac{1}{3}+\int_0^\infty g(\nu)\ln\nu d\nu \bigg/ \int_0^\infty g(\nu)d\nu\right], \tag{5}$$

where k_B is the Boltzmann constant and $\Theta_C(0°)$ is the specific-heat Debye temperature at 0°K. The ν_n-versus-n curves for the two temperatures are shown in Fig. 5. Experimental values for several of the ν_n for copper have been reported by Salter[15] based on an analysis of the specific-heat data reported by Martin[16] and by Franck *et al.*[17] These data were first corrected to correspond to the sample volume at 0°K, so that one would expect the resulting ν_n to be in better agreement with the calculations based on the low-temperature neutron data as illustrated in Fig. 5.

A comparison of the temperature dependences of the frequencies ν_n is shown in Fig. 6 by means of a plot of $\bar{\gamma}(n)$ versus n, where we have defined

$$\bar{\gamma}(n)=-\frac{\Delta\nu_n/\bar{\nu}_n}{\Delta V/\bar{V}}. \tag{6}$$

Here $\Delta\nu_n=\nu_n(49°\text{K})-\nu_n(298°\text{K})$ and $\bar{\nu}_n$ is the average value of ν_n in the 49 to 298°K range; analogously, ΔV and $\bar{V}$ represent the change and average value of the sample volume, respectively. In this temperature range $\Delta V/\bar{V}\simeq 0.01$ for copper.

If the normal mode frequencies depended only on the crystal volume, as assumed in the quasiharmonic model,[18] these $\bar{\gamma}(n)$ would be equal to the $\gamma(n)$ parameters defined by

$$\gamma(n)=-\partial\ln\nu_n/\partial\ln V. \tag{7}$$

Working within the assumptions of the quasiharmonic model, Barron *et al.*[18] show how approximate values for several of the $\gamma(n)$'s can be obtained from analyses of

[14] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).
[15] L. S. Salter, Advan. Phys. **14**, 1 (1965).
[16] D. L. Martin, Can. J. Phys. **38**, 17 (1960).
[17] J. P. Franck, F. D. Manchester, and D. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).
[18] T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, Proc. Roy. Soc. (London) **A279**, 62 (1964).

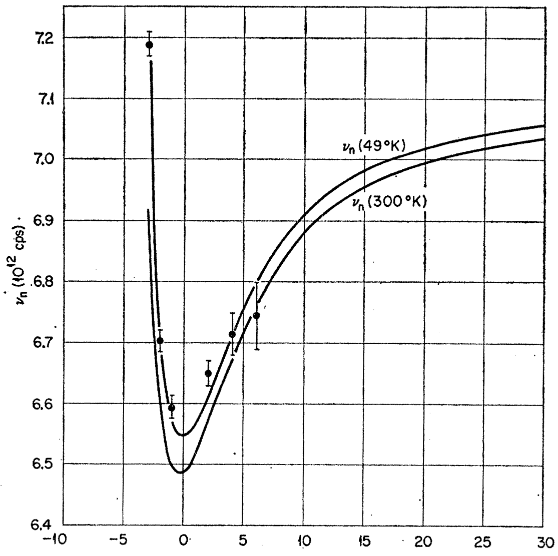

FIG. 5. Debye "cutoff" frequencies ν_n obtained from $g(\nu)$ at 49 and 298°K. The experimental points were taken from Salter (Ref. 15).

the temperature dependence of the Grüneisen parameter $\gamma=\beta V/KC_v$, where β is the volume coefficient of thermal expansion, K the isothermal compressibility, and C_v the specific heat at constant volume. In particular, the high- and low-temperature limits of γ are $\gamma(0)$ and $\gamma(-3)$, respectively.

Obviously, the quasiharmonic model is not valid in general, and the values of the $\bar{\gamma}(n)$ in Eq. (6) will have a contribution from the explicit dependence of the normal mode frequencies on temperature. However,

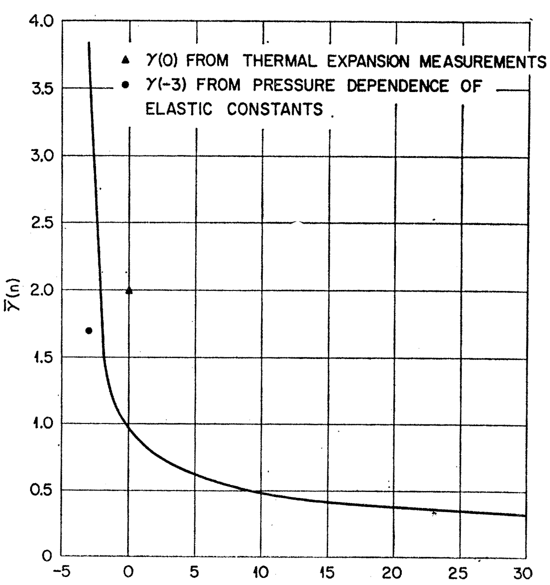

FIG. 6. The $\bar{\gamma}(n)$ obtained from the variation of ν_n with temperature using Eq. (6). $\gamma(0)$ and $\gamma(-3)$ were taken from Ref. 19.

according to Barron,[2] as long as anharmonic effects are not too large, the frequency distribution determined from neutron inelastic scattering measurements is appropriate for the calculation of the entropy S. Since

$$\beta=K(\partial S/\partial V)_T, \tag{8}$$

so that

$$\gamma=(V/C_v)(\partial S/\partial V)_T, \tag{9}$$

one might expect the high- and low-temperature limiting values of γ to provide fair estimates ($\sim$10%) of $\gamma(0)$ and $\gamma(-3)$, respectively, for the $g(\nu)$ obtained from neutron data. That is, even though the $\bar{\gamma}(n)$ will have contributions arising from the dependence of the normal mode frequencies on both volume and temperature, the $\gamma(n)$, as estimated from measurements of γ, may provide reasonably good estimates of only the volume dependence of the $g(\nu)$ moments.

Estimates of $\gamma(-3)$ and $\gamma(0)$ are shown in Fig. 6. Above 150°K, experimental value of γ for Cu is independent of temperature and equal to 2.0.[19] This value is taken to be an estimate of $\gamma(0)$. As seen in Fig. 6, this value for $\gamma(0)$ is considerably larger than $\bar{\gamma}(0)$, suggesting that the explicit temperature dependence of ν_0 is large and tends to cancel the volume dependence. At extremely low temperatures, measurements of β, and hence γ, are very difficult. An alternative and the most direct determination of $\gamma(-3)$ is from measurements of the pressure dependence of the elastic constants. The value of $\gamma(-3)$ obtained by Collins[19] from the data of Daniels and Smith[20] for the variation of room temperature elastic constants as a function of pressure is shown in Fig. 6. Actually, this may not be a reliable estimate of $\gamma(-3)$ if the pressure dependences of the elastic constants of Cu vary with temperature.[21] This value for $\gamma(-3)$ is considerably smaller than $\bar{\gamma}(-3)$ in contrast to the comparison of $\gamma(0)$ and $\bar{\gamma}(0)$.

A comparison between measured values[16,17,22] for the Debye temperature, Θ_C, obtained from specific-heat measurements and those calculated using the two distribution functions in Fig. 3 is shown in Fig. 7. Below about 50°K the curve calculated with the 49° $g(\nu)$ is in excellent agreement with experiment. The changes in the phonon frequencies measured between 298 and 49°K, though quite small, apparently were just those needed to produce almost exact agreement between the calculated and measured values of Θ_C at low temperatures. Such good agreement at low temperatures, also found for Al,[23] is another illustration of the detailed compatibility that can exist between neutron data and thermodynamic data at temperatures where anharmonic effects are small.

At temperatures above 50°K, Curve A remains in better agreement with experiment up to 298°K. How-

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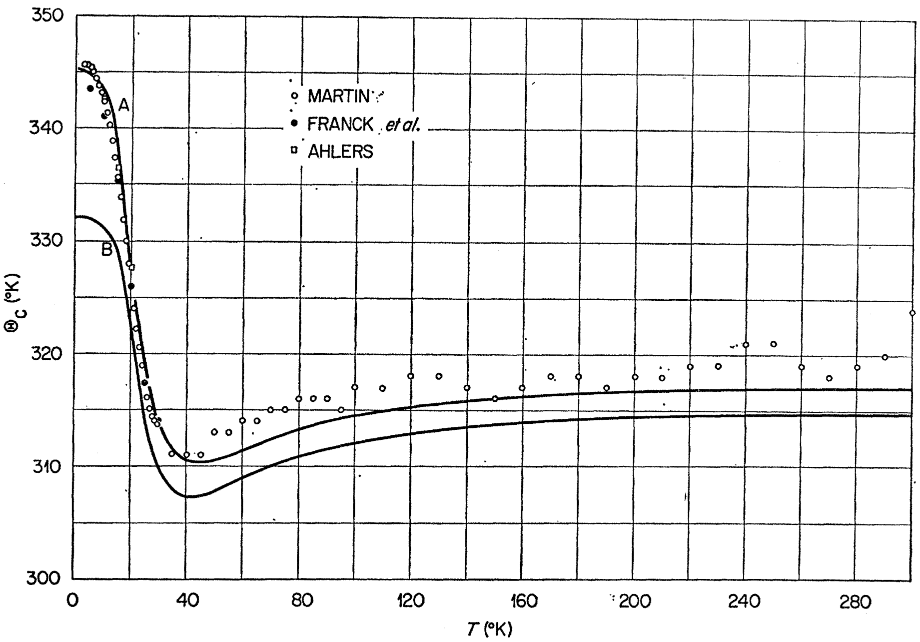

FIG. 7. Comparison of the calculated $\Theta_C(T)$ with experiment. Curves A and B were calculated with $g(\nu)$ at 49 and 298°K, respectively. The experimental results were obtained from Refs. 16, 17, and 22.

ever, this result may not be significant because at higher temperature the experimental values for Θ_C are extremely sensitive to uncertainties in C_v. For example, a 1% change in C_v at 298°K produces about a 10% change in Θ_C. Still, in view of the breakdown of the quasiharmonic model discussed above, the anharmonic contributions to the specific heat data are probably different than one would estimate from a comparison of calculations using the frequency distributions at 49 and 298°K. Thus the frequency distributions obtained from an analysis of the neutron scattering data for Cu are appropriate for the calculation of the entropy S but not necessarily for the specific heat.[2] The entropy at 298°K calculated with the 298°K $g(\nu)$ is 7.86 cal/°K g-at., which is in excellent agreement with the experimental values of 7.92±0.04 cal/°K g-at. reported by Martin.[16] The entropy at 298°K calculated with the 49°K $g(\nu)$ is 7.80 cal/°K g-at. At 49°K the calculated and measured value of the entropy certainly must agree in view of the detailed agreement between the calculated and measured specific heats using the 49°K $g(\nu)$.

SUMMARY

The results presented here show that the temperature dependence of the phonon frequencies in Cu generally decreases with increasing frequency. For the lower frequencies ($\nu \lesssim 3\times10^{12}$ cps), the frequency changes measured between 49 and 298°K are consistent with the 3–4% changes estimated from the isothermal elastic constants.[12] For higher frequencies the relative changes are much smaller, often being 1% or less.

A fairly strong temperature dependence for the widths of some focused phonons was observed. The observed width changes varied significantly with the phonon branch. However, at the present time it is not possible to determine whether it is the temperature dependence of the widths or the widths themselves that have the strong dependence on branch, and further work in this area is anticipated. Because of the large width changes that were observed and the availability of nearly perfect Cu crystals, future investigations of phonon lifetimes in Cu may be quite fruitful.

Both the 49 and 298°K results could be adequately described by AS force constant models with interactions extending to the sixth-nearest neighbors. These models were then used to calculate a frequency distribution function $g(\nu)$ at each temperature. The moments of these distributions lead to values for $\bar{\gamma}(-3)$ and $\bar{\gamma}(0)$ that are in very poor agreement with estimates of $\gamma(-3)$ and $\gamma(0)$, thereby suggesting that Cu does not satisfy the assumptions of the quasiharmonic model.

Using the $g(\nu)$ obtained from the 49°K force constant model, we calculated a Θ_C-versus-T curve which is in excellent agreement (within about 0.5%) with experiment between 0 and 50°K. Above 50°K the Θ_C values calculated with the 49°K $g(\nu)$ remain in better agreement with experiment than those obtained with the 298°K $g(\nu)$. However, the value calculated for the entropy at 298°K with the 298°K $g(\nu)$ agrees better with experiment than that calculated with the 49°K $g(\nu)$, a result which is in agreement with the theoretical predictions of Barron.[2]