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Zero-Sound Elastic Constants of Solid Krypton at $T = 114\,^{\circ}\mathrm{K}$*

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The phonon dispersion of a single crystal of krypton has been measured for the [110]L, [110]T_1, and [100]T modes at $T = 114\,^{\circ}\mathrm{K}$ in the region $0.03 < q < 0.15$ Å^{-1} by the inelastic scattering of neutrons. Analysis of the results based on a nearest-neighbor-force-constant fit gives for the zero-sound elastic constants $C_{11} = (289 \pm 4)$, $C_{12} = (185 \pm 4)$, and $C_{44} = (144 \pm 1) \times 10^8$ dyn cm^{-2}. This results in an anisotropy $A = 2C_{44}/(C_{11} - C_{12}) = 2.76 \pm 0.05$ and a departure from the Cauchy relation of $\delta = (C_{44} - C_{12})/C_{12} = -0.22 \pm 0.02$.

I. INTRODUCTION

Theoretical calculations of the properties of rare-gas solids has progressed considerably in the last decade. Computational capability has been increased and hence calculations need not be restricted to simple interaction potentials of limited validity, i.e., the Lennard-Jones potential. One property of importance is the elastic constants and the present paper is directed towards their measurement in krypton. Such measurements can give a measure of the importance of three-body forces by comparison of the results with calculations which have utilized a suitable two-body potential.[1,2] One indication of three-body effects is the deviation of the Cauchy relation $\delta = (C_{44} - C_{12})/C_{12}$ at liquid-helium temperatures, where departures due to quantum effects have been minimized by the heavy mass of the krypton atom. The three-body effect acts in opposition to the quantum effect and Hüller *et al.*[1] give for krypton, at $T = 0$, a value for δ of $+0.02$ and -0.07 for calculations using a Lennard-Jones potential without and with a three-body force, respectively.

While the measurement of elastic constants on single crystals through the use of ultrasonic transducers is well known, its direct application to the case of rare-gas solids has not been straightforward. The main difficulty is obtaining one oriented single crystal of sample to which transducers can be satisfactorily bonded; the bonding problem as the temperature changes is maximized by the large volume expansivity in these solids. Ultrasonic measurements have been made as a function of temperature for the transverse and longitudinal sound velocities in polycrystalline krypton,[3–6] which alone do not give the elastic constants. Korpiun *et al.*[6] have further used circuitous reasoning to justify the assumption of a measurement in two samples as being made in the [100] direction, thus obtaining C_{11}, C_{44}, and thence C_{12} from the polycrystalline measurements.

Recently Brillouin scattering has been used by Gornall and Stoicheff[7,8] and Stoicheff *et al.*[9] to measure the sound velocities of oriented single crystals of xenon and neon, respectively. The light scattering, however, requires optically uniform surfaces as well as optical quality of the bulk crystal; the measurements at this time have been limited to the triple-point temperature (the growing temperature of the solid). Here, there is the problem of bonding the optical surface of the capillary tube in which the sample grows to the sample. The method has the advantage that x-ray orientation and the light scattering are done on only a small portion of the total sample in the capillary tube and that this portion alone needs to be single crystal.

Another method which also requires only the presence of a large grain in the sample is the inelastic scattering of neutrons. Here the problem has been that measurements must be made at small values of $\vec{q}$ to ensure a reliable determination of the limiting slopes of dispersion curves as $\vec{q} \rightarrow 0$. Additionally, the low-$\vec{q}$ measurements must necessarily be corrected for the systematic effects of instrumental resolution. The first such fully corrected low-$\vec{q}$ measurements have been reported by Peter *et al.*[10] on krypton at $T = 77\,^\circ\mathrm{K}$. The results for C_{11} and C_{44} agree to within two standard deviations of the indicated errors of the ultrasonic data of Korpiun *et al.*[6]; however, a large discrepancy in C_{12} was found. The neutron value of the bulk modulus $B_0 = \frac{1}{3}(C_{11} + 2C_{12}) = (330 \pm 9) \times 10^8$ dyn cm^{-2} was also higher by 25% than the measured thermodynamically related adiabatic bulk modulus, B_s.[11,12]

This difference between B_0 and B_s could well be indicative of a large difference between zero and first sound[13] in krypton at 77 °K, although theoretical estimates put the difference at < 5%.[14,15] It is worth noting that in neon at 5 °K,[16] measurements of B_0 and B_s agree to within 3%, which is the reported accuracy of the measurements. At 5 °K, the difference between zero and first sound is expected to be small as the difference tends to zero at $T = 0$.

As the difference between zero and first sound should be largest at the melting temperature, we have undertaken the measurement of the zero-sound elastic constants at $T = 114\,^\circ\mathrm{K}$ in krypton ($T_m = 116\,^\circ\mathrm{K}$). At this temperature, the various methods should be able to be reliably compared since the light scattering experiments are presently performed near the melting temperature and since the ultrasonic measurements should have minimum bonding problems near T_m.

II. SAMPLES AND METHOD

Previous experimental studies of rare-gas solids by the Brookhaven group[16–18] have concentrated on isochoric studies whereby the samples have been grown at high pressures, typically 1–5 kbar. However, in order to more directly compare the neutron results with those obtained by other methods, in the present instance we have investigated a crystal grown at atmospheric pressure in the manner of Peterson *et al.*[19] Growth was in a Kapton tube (polypyromelitimide film 0.05 mm thick rolled into a cylinder 9 mm i.d. by 20 mm high) which was contained in an isothermal chamber connected to the copper-block base of a variable-temperature cryostat. Temperature control was possible to ± 0.002 °K and a 3.5 °K differential was established across the Kapton cell during growth. After solidifying, the base of the sample was controlled at 113 °K; the top of the cell, however, could only be reduced to 115 °K due to heat conducted down the stainless-steel tubing which supplied the krypton gas into the top of the Kapton cell.

The measurements were performed on a triple-axis spectrometer at the Brookhaven high-flux beam reactor. A [001] zone of scattering was obtained with the Dewar tilted 20° from the growth axis. A neutron Polaroid picture of the (200) reflection showed the cell to be 95–100% one single crystal, and a rocking curve indicated a full width at half-maximum (FWHM) for the mosaic spread of less than 5 min. At 114 °K we found $a = 5.830 \pm 0.002$ Å in agreement with the more accurate work of Losee and Simmons.[20] A cylindrically curved monochromator and a flat analyzer[21,22] of pyrolytic graphite (002) were used with initial neutron energies of 8.5 meV [this was required in order to make some of the required measurements at the Brillouin zone centered on (2, 2, 0)]. A few additional phonons of the [100]T branch measured from (2, 0, 0) were done with $E_0 = 5.5$ meV. All collimators were 10 min for measurement of the [110]T$_1$ modes, while 20 min was used for the [110]L and [100]T modes.

The [110]T$_1$ modes were measured in the constant-$\vec{Q}$ mode of spectrometer operation, whereas the constant-E mode of operation was predominantly utilized for the other two branches. In this regard, it is worth noting that for small-$\vec{q}$ measurements of the longitudinal modes, the constant-E mode of operation appears to be mandatory. The reason is that one observes the response of all modes appropriately weighted with the instrumental resolution. The relatively coarse vertical resolution (here it is 0.06 Å^{-1} FWHM) permits a response to be observed from low-energy modes (primarily from one of the energy surfaces associated with the transverse modes) which is more intense than the desired longitudinal response. In the constant-$\vec{Q}$ scan the longitudinal response is at best a shoulder on the lower-energy peak, whereas in the constant-E scan these low-energy modes are predominantly unobserved.

As the observed peak in a scan is due to a weighted response of all modes within the instrumental resolution,[23] each scan has been analyzed as described by Peter *et al.*[10] in order to find the desired ($\vec{q}$, E)

point of the phonon dispersion. Briefly, a set of Born–von Kármán force constants Φ_i determined from the combined measurements of Daniels *et al.*[17] and Peter *et al.*[10] at 77 °K has been found for the lattice spacing at 114 °K, assuming a Grüneisen $\gamma = 3$, $\Delta\Phi i/\Phi_i = -6\gamma(\Delta a/a)$. These force constants have then been used in a program described by Werner and Pynn[24] which calculates the expected phonon response due to the finite instrumental resolution. The peak in the calculated response can then be compared to the expected value $(\vec{q}, E)$ in the particular direction being measured.

III. RESULTS

Measurements of the $[110]T_1$, $[110]L$, and $[100]T$ branches have been made and the resolution-corrected results are shown in Fig. 1. The errors in most of the measurements are due primarily to the precision with which the instrument could be adjusted; e.g., the analyzer setting could be made with care to the nearest ±0.005°. For the initial energies of 8.5 meV required to measure near (2, 2, 0), this results in a minimum detectable precision in the energy setting of ±0.003 meV and in the $\vec{q}$ setting of ±0.0001 $Å^{-1}$. As the dispersion slopes are less than 10 meV Å, the energy setting is the more important source of error. All measurements are made relative to the Bragg peak position and therefore a minimum error in the measurement of ±0.004 meV might be expected. Some of the higher-energy modes had an additional uncertainty caused by a decreased scattering intensity giving errors of ±0.01 meV.

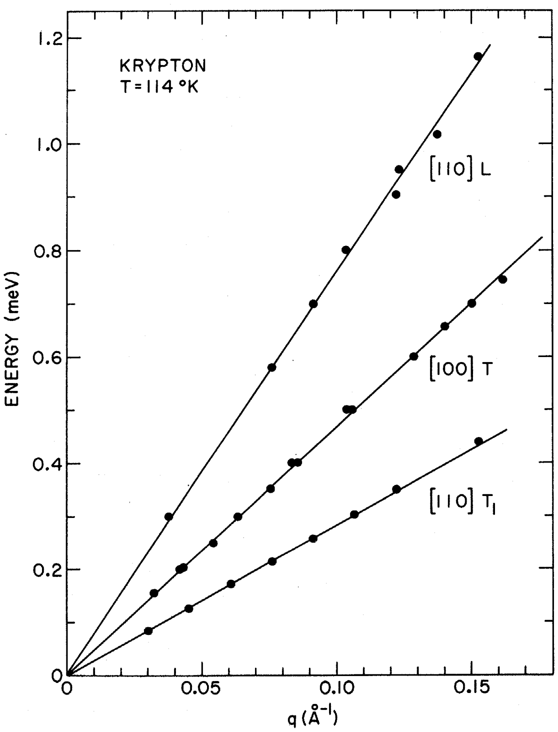

FIG. 1. Krypton phonon dispersion at 114 °K. The errors are about the size of the data points. The solid lines are a nearest-neighbor Born–von Kármán fit to the data. Note that the zone boundary in the [100] direction is at $q = 2\pi/a = 1.078$ $Å^{-1}$.

TABLE I. Elastic constants (10^8 dyn cm^{-2}) of krypton at 114 °K. The present results are in column a, ultrasonic results of Ref. 6 in column b, and theoretical results of Ref. 26 in column c.

	a	b	c
C_{11}	289 ± 4	299	275 ± 6
C_{12}	185 ± 4	107	186 ± 4
C_{44}	144 ± 1	119	127 ± 3
$\frac{1}{2}(C_{11} - C_{12})$	52 ± 1	96	45
$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	380 ± 4	322	357
A	2.76 ± 0.05	1.2	2.86 ± 0.15
δ	−0.22 ± 0.02	+0.11	−0.32
B	219 ± 2	171	216 ± 4

The data have been analyzed in terms of Born–von Kármán force constants using a program written by Svensson *et al.*[25] As the $\vec{q}$ range is quite limited here, only a nearest-neighbor model was calculated, giving an effective force constant fit which is shown by the solid lines of Fig. 1. These force constants have little meaning in themselves, but they do allow the determination of the elastic constants which are given in column a of Table I. The three branches $[100]T$, $[110]T_1$, and $[110]L$ give directly C_{44}, $\frac{1}{2}(C_{11} - C_{12})$, and $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, respectively, and the latter two quantities are also listed along with values of A, δ, and B. All errors are single standard deviations given by least-squares calculations.

The model fit does introduce a specific relation into the second derivative of the dispersion. The second derivative of the $[110]T_1$ branch at finite small $\vec{q}$ is negative here, whereas a combined fit of the data of Daniels *et al.*[17] and Peter *et al.*[10] to a two-nearest-neighbor-force-constant model gives a positive second derivative. We have therefore attempted a more general fit to the data where each branch is fitted to $E = \epsilon + \alpha q + \beta q^3$, where ϵ might relate to a systematic spectrometer mis-set and α relates to the elastic constants. The results are given for all three branches in Table II(a).

It is evident that only the two transverse branches are appropriate for such general analysis. The $[110]L$ branch does not have sufficient low-energy points to find a reasonable value for ϵ. The values of ϵ determined for the two transverse branches are indicative that a systematic deviation of the spectrometer setting was avoided. Table II(b) gives the analysis with $\epsilon = 0$.

It is noted that the second derivative given by

TABLE II. General fit to the data. C represents the particular set of elastic constants giving the slope of each branch. The units are those appropriate for E in meV and q in Å^{-1}; C is in units 10^8 dyn cm^{-2}.

	ϵ	α	β	C
(a) Data fit to $E=\epsilon+\alpha q+\beta q^3$				
[100]T	0.001 ± 0.006	4.72 ± 0.10	-2.7 ± 3.1	144 ± 6
$[110]\text{T}_1$	-0.002 ± 0.002	2.82 ± 0.03	3.7 ± 1.1	51 ± 1
[110]L	-0.016 ± 0.07	8.19 ± 1.0	-31 ± 29	435 ± 100
(b) Data fit to $E=\alpha q+\beta q^3$				
[100]T		4.73 ± 0.03	-3.1 ± 1.6	145 ± 2
$[110]\text{T}_1$		2.78 ± 0.01	4.9 ± 0.7	50 ± 1
[110]L		7.97 ± 0.22	-25 ± 14	412 ± 23
(c) Data fit to $E=\alpha q$				
[100]T		4.69 ± 0.01		143 ± 1
$[110]\text{T}_1$		2.84 ± 0.01		52 ± 1
[110]L		7.60 ± 0.05		374 ± 5

$6\beta q$ would be positive for the $[110]\text{T}_1$ branch at finite q. Comparing the results of Table II(b) with Table Ia, the elastic constant combinations relating the slopes of the various branches are nearly unchanged for the two transverse branches. While the values for the [110]L branch overlap with respect to their errors, it is felt that the general fit finds too large a value of $\beta=-25\pm14$ meV Å^3 to be physically acceptable when compared to the size of the cubic term in the transverse branches. The large uncertainties also evidence the difficulty of treating the data of [110]L too generally. For completeness, the results of a linear fit are included in Table II(c).

IV. DISCUSSION

A general fit to the data indicates the values in column a of Table I obtained from an effective nearest-neighbor-force-constant fit are reasonable, although the value of $\frac{1}{2}(C_{11}-C_{12})$ is more probably given by the general fit as $(50\pm1)\times10^8$ dyn cm^{-2}. The positive value of β found for $[110]\text{T}_1$ as shown in Table II(b) is similar to a finding in krypton at 77 °K; the ratio β/α has increased from 0.4 Å^2 at 77 °K to 2 Å^2 at 114 °K. A positive value for β also is found in the $[110]\text{T}_1$ branch of neon at 5 °K.[16]

We show the values of Korpiun *et al.*[6] obtained by ultrasonic methods in column b of Table I. Theoretical calculations by Klein and Murphy[26] using a Monte Carlo technique with a Bobetic-Barker pair potential and including three-body forces is given in column c of Table I. The theoretical fit is really quite a good save for C_{44}. Additional values of B_s obtained from ultrasonic data on polycrystals are (204 ± 11) and $(197\pm10)\times10^8$ dyn cm^{-2} by Kupperman and Simmons[4] and Bezuglyi *et al.*,[5] respectively.

It is noted that whereas the latter two measurements are in agreement within their indicated errors, there did exist a systematic difference between the two investigations over the temperature range at which the measurements overlapped. These two measurements also differ considerably from the work of Korpiun *et al.*[6] The application of the ultrasonic method which superficially should be of high accuracy (< 0.5%) is seen to be quite difficult in the case of krypton. It is difficult to judge, therefore, whether the difference between zero and first sound, as evidenced by columns a and b in Table I, is real. This difference is more directly in doubt when one considers that the orientation of the single-crystal ultrasonic measurements[6] was not determined. The 10% difference between B_0 in column a of Table I with B_s[4,5] is much less than at $T=77$ °K, where a 25% difference was found between B_0[10] and an adiabatically corrected B_T.[12]

Light scattering measurements on krypton comparable to the work on xenon[7,8] and neon[9] might well be expected shortly with which the present measurements done at 114 °K could be directly compared.[27] However, a clear definitive difference between zero and first sound appears to demand comparison with ultrasonic data. The energies involved in the three methods are 10^7, $2-4\times10^9$, and $0.5-4\times10^{12}$ Hz for ultrasonic, light scattering, and neutron diffraction, respectively. The specific location of the transition region between zero and first sound could affect an interpretation of the light scattering results, although if the total difference between zero and first sound is < 5%, such details may not be explorable within the accuracy of the measurements.

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Theory of Thermal Conductivity of Anharmonic Crystals

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The thermal conductivity κ of an anharmonic crystal is calculated based on the Green–Kubo linear-response theory, using the Zwanzig–Mori projection-operator method. The appropriate heat-current autocorrelation function is determined in the Van Hove long-time weak-coupling limit and is shown to be real and of exponential form. The final result for κ has the well-known Debye–Peierls form, as expected. The relaxation time is shown to be the half-interval Fourier transform of the time correlation of a function which describes linear coupling of the phonon modes averaged over the harmonic lattice.

I. INTRODUCTION

The purpose of this work is to present a theory of the thermal conductivity of an anharmonic crystal based on the Green–Kubo linear-response theory, using the Zwanzig–Mori projection-operator method. The final result for the thermal conductivity is the famous Debye–Peierls form in terms of phonon relaxation times.

As early as 1914 Debye[1] succeeded in identifying anharmonicity as the primary mechanism of thermal resistance in insulators. He was also successful in providing on phenomenological grounds, through classical theory, the general form for the thermal conductivity in terms of relaxation times. His result awaited theoretical justification by Peierls[2] fifteen years later.

Peierls derived a quantum-mechanical transport equation for the phonon distribution function for a crystal with cubic anharmonicity and obtained the solution which led directly to Debye's expression for the lattice thermal conductivity.

The present approach leads in a natural way to a microscopic picture of phonon relaxation times. In fact we shall show that these times can be expressed quite simply as Fourier transforms of the time correlation of a function which describes linear coupling of the phonon modes [Eq. (3)] averaged over the harmonic lattice [Eq. (24)].

After introduction of the system Hamiltonian with special attention given to the motivation for choice of form, we state the Green[3]–Kubo[4] expression for the thermal conductivity in a form well suited to the present work in terms of the heat-current autocorrelation function. Next the usual Peierls[2] heat-current expression in terms of the so-called phonon occupation numbers N_k is used to express the heat-current autocorrelation function between two modes k and k', $C_{kk'}(t) \equiv \langle \delta N_k \delta N_{k'}(t) \rangle$, where δN_k is the deviation of N_k from its mean value. After introducing a projection operator well suited to the present problem of the form

$$P_k X = \delta N_k \langle \delta N_k X \rangle / \langle \delta N_k \delta N_k \rangle ,$$