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Elastic constants of krypton single crystals determined by Brillouin scattering*

D. Landheer,† Howard E. Jackson,‡ R. A. McLaren,§ and B. P. Stoicheff
Department of Physics, University of Toronto, Toronto, Ontario, M5S 1A7, Canada

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Single crystals of krypton were grown at 115.6 K; Brillouin spectra of two such crystals were investigated for several orientations. All three Brillouin components expected for a cubic crystal were observed and their frequency shifts were used to evaluate the adiabatic elastic constants: $C_{11} = 26.57 \pm 0.30$, $C_{12} = 17.25 \pm 0.20$, $C_{44} = 12.61 \pm 0.15$, in kbar. These values lead to an adiabatic bulk modulus $B_S = 20.36 \pm 0.22$ kbar, and to an anisotropy parameter $A = 2.704 \pm 0.013$. The available theoretical values, whether based on a Mie-Lennard-Jones (6-12) potential or on a more refined pair potential, are not in agreement with the present elastic constants. A comparison of these values with the elastic constants determined from recent neutron-scattering experiments shows differences as large as 12%. It is suggested that these differences arise from the different velocities of zero and first sound in this temperature region of large anharmonicity. An analysis of the relative intensities of the Brillouin components yielded the ratios $p_{12}/p_{11} = 1.00 \pm 0.08$ and $p_{44}/p_{11} = 0.11 \pm 0.01$ for the Pockel's coefficients.

I. INTRODUCTION

The present investigation of the Brillouin spectrum of solid krypton is a continuation of a recent series of experiments from this laboratory which have led to the evaluation of the elastic constants of solid xenon,[1] argon,[2,3] and neon.[2,4] As in the earlier work, single crystals were grown from the liquid; their orientations were determined by Laue x-ray diffraction in transmission; and Brillouin spectra excited by laser radiation were recorded at high resolution. For krypton, all three Brillouin components expected for a cubic crystal were observed for almost all orientations of the crystals, in contrast to the spectra of xenon, argon, and neon, which usually exhibited the longitudinal and only one of the transverse components. Two single crystals of krypton were selected for detailed study. Analyses of their Brillouin shifts gave accurate values of all three adiabatic elastic constants C_{11}, C_{12}, and C_{44}; analyses of their relative intensities yielded values for the ratios of the elasto-optic coefficients p_{12}/p_{11} and p_{44}/p_{11}.

While this work was in progress, Skalyo and Endoh[5] reported their results of the elastic constants at 114 K, based on accurate measurements of dispersion curves obtained by neutron scattering. These two investigations have provided the first opportunity for direct comparison of the elastic constants of a rare-gas solid determined by Brillouin and neutron scattering. The results[6] indicate a much larger difference than expected from available theories.

II. EXPERIMENTAL METHOD

A detailed description of the apparatus and experimental technique has already been given in an earlier paper[4] on neon. The only change was to replace the coolant from liquid helium for neon to liquid nitrogen for krypton. (Thus the cold-finger at the bottom of the reservoir, which cooled the sample by conduction, was kept full of liquid nitrogen and maintained at 77 K.)

Single crystals of krypton were grown, as before, with a temperature gradient of ~ 1 K between the bottom and top of the sample cell, and the temperature at the center of the cell was maintained at 115.6 ± 0.2 K, close to the triple-point temperature of 115.8 K. In all, ten different single crystals having random orientations were grown. Two of these were chosen for this study.

Brillouin spectra were excited by ~ 17 mW of 4879.9-Å radiation (from an Ar$^+$ laser) incident vertically along the cell axis. The incident radiation was polarized perpendicular to the scattering plane, and the spectrometer collected the total scattered intensity at 90° within a solid angle of 5×10^{-4} sr. The Fabry-Perot spectrometer was the same as described in Ref. 4, but the interferometer had a different mirror separation, namely, 14.874 ± 0.02 mm, giving a spectral free range of 10.078 ± 0.026 GHz. The mirror reflectivity was 98.8%, and a finesse of better than 60 was easily maintained over periods of several hours. Each spectrum was scanned at the rate of 1 Hz, and the signals accumulated for periods of 15 min. to 1 h.

III. EXPERIMENTAL RESULTS

A. Brillouin spectra

Brillouin spectra of the two crystals were recorded at ~ 5° intervals of rotation about the vertical cell axis. Seventeen spectra of crystal No. 1 were obtained, and 18 of crystal No. 2. In almost all spectra, the longitudinal and both transverse components were observed. A typical spectrum is reproduced in Fig. 1. It shows an intense component at the incident frequency ν_L (due primarily to stray light scattered from crystal imperfections),

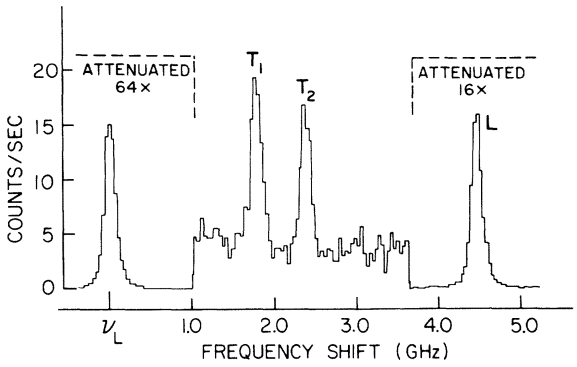

FIG. 1. Typical Brillouin spectrum of a Kr single crystal at a temperature of 115.6 K. (Only the Stokes side is shown.)

and all three Brillouin components, one arising from scattering by longitudinal phonons (L) and two less-intense components that are due to transverse phonons (T_1, T_2).

In Table I are given the frequency shifts of the Brillouin components, and the ratios of the integrated intensities of the T_1 and T_2 components relative to the L component, for various rotations of the two crystals about the cell axis. (Such rotations should ideally involve only changes in ϕ; however, owing to a slight wobble of the cell with respect to the vertical axis defined by the laser beam, cell rotations also resulted in slight variations in θ and χ.)

The quoted errors in the frequency shifts arise from two sources. One is the possible error in

TABLE I. Measured Brillouin shifts (in GHz) and intensity ratios as a function of crystal orientation.

θ	ϕ	χ	$\nu(L)$	$\nu(T_1)$	$\nu(T_2)$	$I(T_1)/I(L)$	$I(T_2)/I(L)$
Crystal No. 1							
−84.2	80.6	−27.9	4.028	2.308	2.640	0.125	0.023
−85.3	76.4	−28.3	4.020	2.315	2.591	0.141	0.031
−83.7	70.4	−27.6	4.035	2.317	2.565	0.147	0.025
−84.3	67.3	−27.6	4.056	2.313	•••	0.185	0.028
−84.6	62.5	−27.7	4.080	2.265	•••	0.220	•••
−85.0	57.4	−27.8	4.117	2.183	•••	0.250	•••
−84.5	52.3	−27.3	4.145	2.097	2.553	0.192	0.016
−85.3	47.5	−27.9	4.184	1.990	2.593	0.163	0.014
−85.2	42.6	−27.8	4.203	1.907	2.596	0.153	0.015
−84.8	37.5	−27.2	4.235	1.835	•••	0.159	•••
−84.7	33.2	−26.7	4.258	1.799	•••	0.123	•••
−85.2	30.9	−27.4	4.274	1.771	•••	0.110	•••
−85.3	26.1	−27.5	4.303	1.714	•••	0.078	•••
−85.6	21.5	−28.0	4.336	1.693	2.582	0.039	0.023
−85.6	15.9	−27.9	4.365	•••	•••	•••	•••
−85.7	11.6	−27.4	4.391	•••	2.461	•••	0.404
−85.8	6.0	−28.0	4.428	•••	2.382	•••	0.045
Crystal No. 2							
−163.1	111.2	119.8	4.322	1.656	2.627	0.033	0.019
−164.1	110.9	122.1	4.331	1.656	2.618	0.026	0.014
−163.8	105.7	121.8	4.333	1.643	2.621	0.020	0.021
−164.0	101.0	122.2	4.357	•••	2.603	•••	0.024
−163.7	96.6	122.4	4.369	•••	2.554	•••	•••
−162.4	92.0	122.8	4.388	•••	2.517	•••	0.039
−164.0	87.6	123.5	4.402	1.680	2.448	0.0163	0.052
−164.3	83.0	123.5	4.418	2.698	2.410	0.030	0.046
−164.4	78.2	123.4	4.431	1.767	2.359	0.047	0.036
−163.6	76.4	124.4	4.429	1.772	2.339	0.060	0.041
−164.0	69.2	124.2	4.434	1.860	2.263	0.097	0.021
−164.4	66.8	123.7	4.440	1.880	2.271	0.105	•••
−164.1	64.6	124.3	4.418	1.875	2.230	0.132	•••
−165.4	57.7	121.5	4.416	1.896	2.274	0.145	•••
−164.8	54.7	123.9	4.390	1.858	2.328	0.108	0.047
−164.8	49.6	123.6	4.357	1.844	2.425	0.094	0.061
−165.2	44.6	122.6	4.348	1.813	2.461	0.070	0.042
−164.3	42.6	126.0	4.309	1.794	2.519	0.077	0.036

measurement of the shifts because of nonlinearities in the scanning of the spectrum and lack of complete resolution of the peaks. This accounts for ~0.7% error in $\nu(\mathrm{L})$ and 1–2% error in $\nu(T_1)$ and $\nu(T_2)$, estimated from variations in the measured frequency shifts for the Stokes and anti-Stokes peaks (recorded over the 1.7 spectral-free-range scan of each spectrum). The second source of error is due to a possible error in orientation of the crystal. An estimate of such errors was made for each orientation as follows: Preliminary values of the elastic constants were used to calculate the frequency shifts for all combinations of the Euler angles which fitted the positions of each x-ray diffraction spot to within the measured accuracy of 0.5 mm. The range of variation of each calculated frequency shift was then taken to be the effective error of that shift.

Similarly, the errors quoted in Table I for the intensity ratios also arise from measurement errors in the recorded spectra and from possible errors in crystal orientation. These were estimated in the same way as the errors in the frequency shifts.

B. Elastic constants

The velocities v_i of the T_1, T_2, and L components of sound for the crystal orientations given in Table I were obtained from the measured frequency shifts $\Delta\nu_i$, by the well-known Brillouin equation

$$\Delta\nu_i = \pm 2\,(n/\lambda)\; v_i \,\sin \tfrac{1}{2}\theta \;.$$

Here, the incident wavelength λ is 4879.9 Å, the scattering angle θ is $90° \pm 15'$, and the refractive index n is $1.3487 \pm (2\times 10^{-4})$, found by interpolation of the measurements by Sinnock and Smith[7] to $T = 115.6$ K.

Values of the three adiabatic elastic constants were determined from these velocities by the method discussed in Ref. 1. Briefly, they were determined by finding the roots of the secular equation

$$|\, \Lambda_{ij} - \rho v^2 \delta_{ij} \,| = 0 \;,$$

with

$$\begin{aligned}\Lambda_{ij} &= (C_{11} - C_{44})\,\chi_i^2 + C_{44}, \quad i = j \;, \\ &= (C_{12} + C_{44})\,\chi_i \chi_j \;, \quad i \neq j \;.\end{aligned}$$

Here the χ_1, χ_2, χ_3 are the direction cosines for the direction of propagation of the sound wave probed in a particular spectrum. The crystal density ρ was taken to be 2.794 ± 0.003 g/cm^3 by extrapolating linearly to 115.6 K the measurements of Korpiun and Coufal.[8]

TABLE II. Elastic constants (in kbar) of krypton at 115.6 K.

	C_{11}	C_{12}	C_{44}	N^a
Crystal No. 1	26.55 ± 0.06	17.18 ± 0.05	12.61 ± 0.04	40
Crystal No. 2	26.61 ± 0.07	17.30 ± 0.06	12.60 ± 0.04	51
Crystals Nos. 1 and 2	26.57 ± 0.05	17.25 ± 0.04	12.61 ± 0.03	91

[a] The number of measured frequency shifts used in each determination of the constants is given by N.

The "best" values of the elastic constants were found by a least-squares method (described in Sec. III B of Ref. 4) using the data of each crystal separately, and for the data of both crystals. The resulting values are given in Table II along with the corresponding single standard-deviation errors. It is seen that the values of C_{11} and C_{44} agree within the stated errors, and the values of C_{12} within two standard deviations. In evaluating the accuracy of these constants, an additional systematic error of 0.85% was added, because of estimated uncertainties in experimental values of refractive index, density, scattering angle, and spectral free range of the interferometer. The final values for the adiabatic elastic constants of krypton under its own vapor pressure at 115.6 ± 0.2 K, obtained in this experiment, are

$$C_{11} = 26.57 \pm 0.30 \text{ kbar} \;,$$

$$C_{12} = 17.25 \pm 0.20 \text{ kbar} \;,$$

$$C_{44} = 12.61 \pm 0.15 \text{ kbar} \;.$$

The agreement of these constants with the original experimental data, that is, the measured Brillouin shifts, may be assessed from the graphs of Fig. 2. Here are plotted the experimental measurements with their errors, and the calculated frequency shifts based on the above values of the elastic constants. It is seen that the agreement is very good for the data of both crystals.

Two quantities related to the elastic constants are of particular interest, namely, the bulk modulus $B_S = \frac{1}{3}(C_{11} + 2C_{12})$ and the Zener anisotropy parameter $A = 2C_{44}/(C_{11} - C_{12})$. These quantities and their errors were calculated from the above constants and the error matrix described in Ref. 4. The values for the adiabatic bulk modulus and anisotropy parameter of krypton at 115.6 K are found to be

$$B_S = 20.36 \pm 0.22 \text{ kbar} \;, \quad A = 2.704 \pm 0.013 \;.$$

The error quoted for B_S includes the systematic error mentioned above, but the error for A is a single standard-deviation error only, since A is a ratio of elastic constants, and is thus independent of the type of systematic error assumed in this experiment.

C. Ratios of Pockel's coefficients

The intensity ratio of two Brillouin peaks is given by

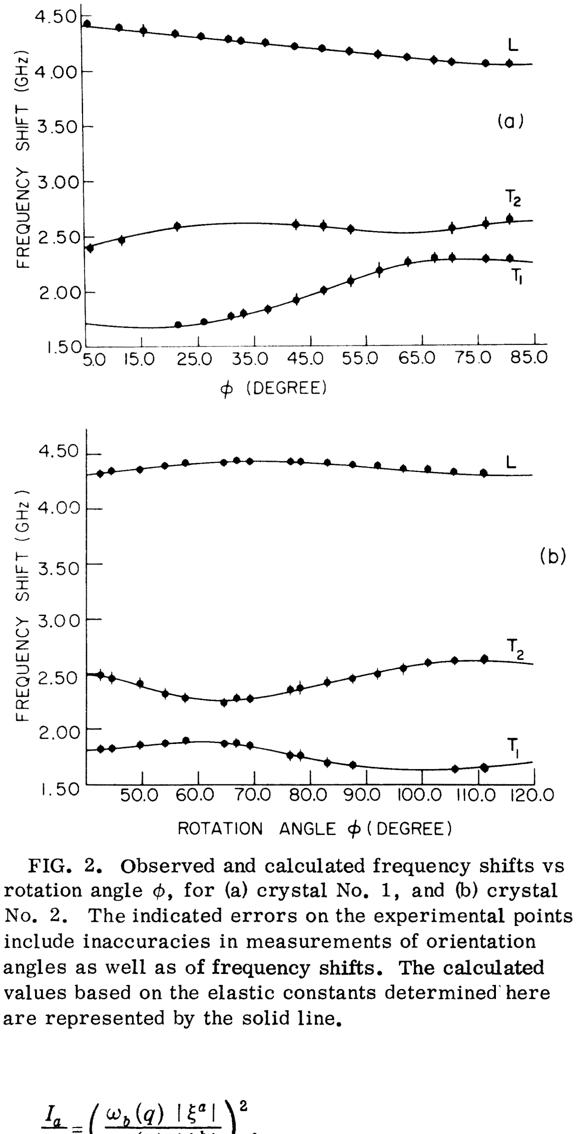

FIG. 2. Observed and calculated frequency shifts vs rotation angle ϕ, for (a) crystal No. 1, and (b) crystal No. 2. The indicated errors on the experimental points include inaccuracies in measurements of orientation angles as well as of frequency shifts. The calculated values based on the elastic constants determined here are represented by the solid line.

$$\frac{I_a}{I_b} = \left(\frac{\omega_b(q)\,|\xi^a|}{\omega_a(q)\,|\xi^b|}\right)^2,$$

where ω_a and ω_b are the two frequency shifts, and the ξ^a and ξ^b are related to the Pockel's coefficients p_{11}, p_{12}, and p_{44} through Eq. (19) of Ref. 1.[9] Thus, these intensity ratios are solely functions of the three elastic constants and the two ratios of the Pockel's coefficients p_{44}/p_{11} and p_{12}/p_{11}. Values of these ratios were determined from the measured intensity ratios (given in Table I) by a least-squares method which is completely analogous to the method used for the elastic constants. The ratios (and their single standard-deviation errors) determined for each crystal and for the two together are given in Table III. Since the results based on the separate crystals are consistent to within three standard deviations, the final result is quoted with this large error. A small systematic error arising from the uncertainties in the elastic constants has also been included; this was determined numerically by varying the elastic constants and noting how the best-fit ratios changed. The ratios of the Pockel's coefficients for krypton at 115.6 K obtained here are

$$p_{12}/p_{11} = 1.00 \pm 0.08, \quad p_{44}/p_{11} = 0.11 \pm 0.01 \;.$$

TABLE III. Ratios of the Pockel's coefficients of krypton at 115.6 K.

	p_{12}/p_{11}	p_{44}/p_{11}	N^a
Crystal No. 1	0.95 ± 0.036	0.12 ± 0.005	24
Crystal No. 2	1.01 ± 0.024	0.11 ± 0.004	29
Crystals Nos. 1 and 2	1.00 ± 0.020	0.11 ± 0.003	53

[a] The number of measured intensity ratios used in each determination is given by N.

In Fig. 3 are shown the two intensity ratios $I(T_1)/I(L)$ and $I(T_2)/I(L)$, calculated from the above values of the Pockel's coefficients, as a function of rotation angle ϕ, for each crystal. It is seen that the agreement with the observed intensity ratios is good.

IV. DISCUSSION AND CONCLUSIONS

A. Ratios of Pockel's coefficients

The ratios of the elasto-optic constants of krypton ($p_{12}/p_{11} = 1.00 \pm 0.08$, $p_{44}/p_{11} = 0.11 \pm 0.01$) are

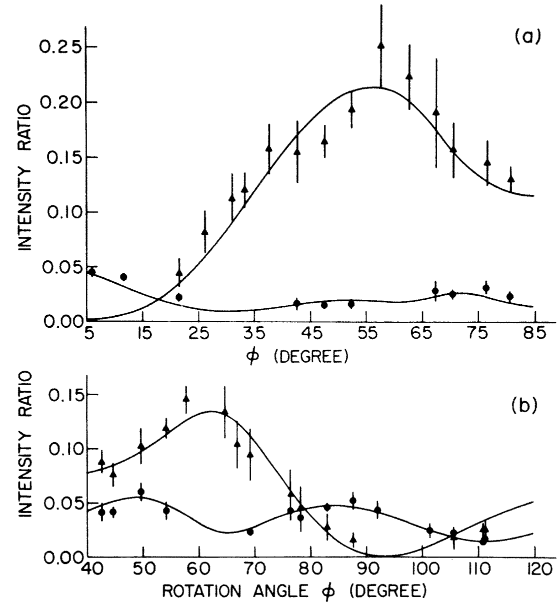

FIG. 3. Intensity ratios of the Brillouin components in the spectra of (a) crystal No. 1, and (b) crystal No. 2, vs rotation angle ϕ. The points with error bars are experimental ratios from the I_v^{Total} spectra: the triangles (▲) represent the ratios $I(T_1)/I(L)$ and the circles (●) represent $I(T_2)/I(L)$. The calculated values of these ratios, based on the Pockel's coefficient ratios determined here, are shown by the solid lines.

similar to those obtained for argon[3] (0.98 ± 0.15 and 0.12 ± 0.05, respectively) but differ from the ratios found for xenon[1] (1.45 and −0.10, respectively). For neon,[4] the intensity ratios can be fitted with a wide range of values: at one extreme, the ratios compare with those of xenon; at the other, the ratios compare well with those of argon and krypton. However, the values for neon and xenon are not as accurate as those for krypton or argon, and a redetermination of the elasto-optic coefficients of the former two solids is necessary before a general conclusion on the relation of the elasto-optic constants of the rare-gas solids can be made.

Werthamer[10] has proposed a mechanism for light scattering in which neutral but polarizable atoms interact via induced-dipole–dipole interactions. While this theory was originally developed to explain the observed intensities for solid helium, Werthamer also tested it against the observed Pockel's coefficients in solid xenon, without success. One result of the theory is the relation

$$1 - p_{12}/p_{11} + 3\, p_{44}/p_{11} = 0 \quad .$$

None of the Pockel's coefficient ratios obtained so far for the rare-gas solids near their triple points fit this relation. This is also true of the present results for krypton, which lead to a value of 0.33 ± 0.10 for this relation.

B. Elastic constants: Comparison of available experimental values

There have been few determinations of the elastic constants of krypton to date. However, several measurements of the bulk modulus and related properties have been made, and these may be compared with the values determined by the present Brillouin-scattering experiments.

The adiabatic sound velocities of polycrystalline krypton have been determined by ultrasonic experiments performed at several laboratories. From these velocities the adiabatic bulk modulus has been calculated using the relation

$$B = \rho\,(v_l^2 - \tfrac{4}{3}\, v_t^2) \quad ,$$

which is valid for an isotropic solid. Kupperman and Simmons[11] have measured the sound velocities by the pulse-echo technique in the temperature ranges 52–115 K for v_l and 95–115 K for v_t. They found a bulk modulus of 20 ± 0.1 kbar at 115 K, in excellent agreement with the present value of 20.4 kbar. Bezuglyi *et al.*[12] have made measurements of the sound velocities in the ranges 20–110 K for v_l and 10–100 K for v_t. Their results are systematically lower than, but within experimental error of, the results of Kupperman and Simmons. Korpiun *et al.*[13] have measured the velocities in the temperature range 4–110 K, and have found good agreement with the other two groups. They have also reported values of C_{11} and C_{44} determined by measuring ultrasonic velocities in "probably single crystals... probably in the ⟨100⟩ direction." As estimated from their graph, they find $C_{11} = 30.0 \pm 3.6$ kbar and $C_{44} = 12.0 \pm 1.4$ kbar at 115 K. These values agree (within their rather large errors) with the present values.

Values of the adiabatic bulk modulus may also be obtained from measurements of the isothermal compressibility χ_T, according to the relation

$$1/B_S = \chi_S = \chi_T - \beta^2 VT/C_p .$$

At 115 K, a calculated value of $\beta^2 VT/C_p = (3.19 \pm 0.08) \times 10^{-11}$ cm^2/dyn is obtained, based on the following values: volume expansivity[14] $\beta = (182 \pm 1) \times 10^{-5}$ K^{-1}, molar volume[14] $V = 29.96 \pm 0.12$ cm^3/mole, and specific heat at constant pressure[15] $C_P = (35.79 \pm 0.18) \times 10^7$ erg/mole K.

Urvas *et al.*[16] have made isothermal compressibility measurements over the temperature range 4–90 K by measuring the change of x-ray lattice parameter with pressure and temperature. Korpiun and Coufal[14] have determined the bulk isothermal compressibility to 1% accuracy by interferrometrically measuring the change in length of a crystal with applied pressure. Their results (while much more accurate) are consistent with the results of Urvas *et al.*,[16] and they cover the temperature range 4–115 K. At 115 K they report a bulk isothermal compressibility $\chi_T = (8.83 \pm 0.10) \times 10^{-11}$ cm^2/dyn. With the bulk adiabatic isothermal correction, this gives an adiabatic bulk modulus of 17.7 ± 0.6 kbar, which is considerably lower than the Brillouin scattering value of 20.4 kbar.

There has been some discussion in the literature[14,17] concerning the effects of thermal vacancies on the high-temperature bulk properties of solid krypton. It has been shown that above 80 K, the vacancy concentration is not negligible and rises to ~0.3% at the triple point. However, Brillouin scattering and ultrasonic measurements should not be very sensitive to the presence of vacancies if the vacancy concentration does not change during the period of a sound wave,[13] and these measurements probably provide elastic constants and bulk moduli close to the "perfect-lattice" values. For example, Pistorius[18] has predicted that the effect of vacancies would be to lower the elastic constants by about two or three times the equilibrium vacancy concentration, which is a negligible effect (< 1%).

Several groups have used neutron-scattering techniques to measure the dispersion curves of krypton at various temperatures. Daniels *et al.*[19] measured the dispersion curves for the ⟨100⟩ and ⟨111⟩ branches of a single crystal of krypton at 79 K and 0.3 kbar. Peter *et al.*[20] made low-q measurements on a free standing single crystal

TABLE IV. Summary of experimental and theoretical values of the adiabatic elastic constants, bulk modulus, and anisotropy parameter, for krypton.

	Temp. (K)	C_{11} (kbar)	C_{12} (kbar)	C_{44} (kbar)	B_S (kbar)	A
Theoretical values						
Lattice dynamics, with three-body forces, Ref. 27	0	50.6	28.7	27.3	36.0	2.47
Quasiharmonic approx. (all-neighbor interactions), Ref. 26	115	29.3	18.7	13.4		
Monte Carlo calculation, Ref. 29	115	27.6 ± 0.6	18.6 ± 0.4	12.7 ± 0.3	21.6 ± 0.4	2.86 ± 0.15
Experimental values						
Neutron scattering, Ref. 25	10	51.4 ± 0.5	28.4 ± 0.6	26.8 ± 0.3	36.1 ± 0.5	2.33 ± 0.05
Neutron scattering, Ref. 20	77	42.5 ± 1.0	28.2 ± 1.2	20.4 ± 0.3	33.0 ± 0.9	2.85
Neutron scattering, Ref. 5	114	28.9 ± 0.4	18.5 ± 0.4	14.4 ± 0.1	21.9 ± 0.2	2.76 ± 0.05
Brillouin scattering, present results.	115.6	26.57 ± 0.30	17.25 ± 0.20	12.61 ± 0.15	20.36 ± 0.22	2.704 ± 0.013

at 77 K, along the ⟨100⟩ and ⟨110⟩ directions. Their high-accuracy measurements allowed them to determine the elastic constants of krypton from the slopes of the dispersion curves, and their results are shown in Table IV. Their bulk modulus is 22% higher than the adiabatic bulk modulus derived by Korpiun and Coufal[14] from the isothermal bulk modulus, and Peter *et al.* suggest that the discrepancy is due to a real difference between zero and first-sound bulk moduli.

Recently, Skalyo and Endoh[5] have made very accurate measurements of dispersion curves in the ⟨110⟩ and ⟨100⟩ directions on single crystals of krypton at 114 K. Their measurements were at low values of q, corresponding to frequencies in the range 25–250 GHz, and the resulting values of the elastic constants are shown in Table IV.

There are significant differences between the elastic constants determined by the neutron and light scattering experiments[6]: the Brillouin results are lower by 8.3% for C_{11}, 7.0% for C_{12}, and 12.6% for C_{44}. These large differences can be attributed to the difference in zero- and first-sound propagation. As pointed out by Cowley[21] (and observed[22] in KBr and in quartz), anharmonicity affects the propagation of sound differently in the low-frequency (first-sound, or hydrodynamic) and high-frequency (zero-sound or collisionless) regimes. Sound waves of frequency ω, such that $\omega\tau_{\text{th}} < 1$ (where τ_{th} is the lifetime of the dominant thermal phonons) are in the first-sound regime; sound waves for which $\omega\tau_{\text{th}} > 1$ are in the zero-sound regime. An estimate of $1/\tau_{\text{th}}$ can be obtained from the work of Niklasson,[23] who has calculated τ_{th} for argon using a phonon-Boltzmann-equation approach. For argon near the triple point, he found $1/\tau_{\text{th}} \sim 3 \times 10^{12}$ Hz. If this value is adopted for krypton, it would indicate that the Brillouin-scattering measurements, which were made at frequencies of 1.7–4.4 GHz, are in the first-sound regime, giving a true measure (with the ultrasonic experiments) of the adiabatic elastic constants. The neutron scattering measurements, however, were carried out at higher frequencies (25–250 GHz) and thus are thought to give zero-sound elastic constants. The frequencies probed by the two experiments differ by at least a factor of 10, and the differences in the elastic constants are in the direction predicted by theory.[21]

The differences found, however, are much larger than expected. Goldman *et al.*[24] have calculated the zero- and first-sound elastic constants of krypton using a self-consistent phonon theory with a Lennard-Jones 6-12 potential. They report differences <4%. Niklasson[23] has calculated the differences in argon to be <4%. These depend strongly on the anharmonic part of the interaction potential; hence the small predicted differences may arise from an inadequate form for the potential used in the calculations and an inadequate treatment of the large anharmonicity characteristic of krypton near the triple point.

The bulk modulus determined by Skalyo and Endoh[5] is 7.4% higher than that determined in the present experiments, as shown in Table IV. In view of this, the differences between the neutron and static bulk moduli at 77 K mentioned previously seem very large. Recently, Skalyo *et al.*[25] have made neutron scattering measurements of the elastic constants of krypton at 10 K. Their bulk

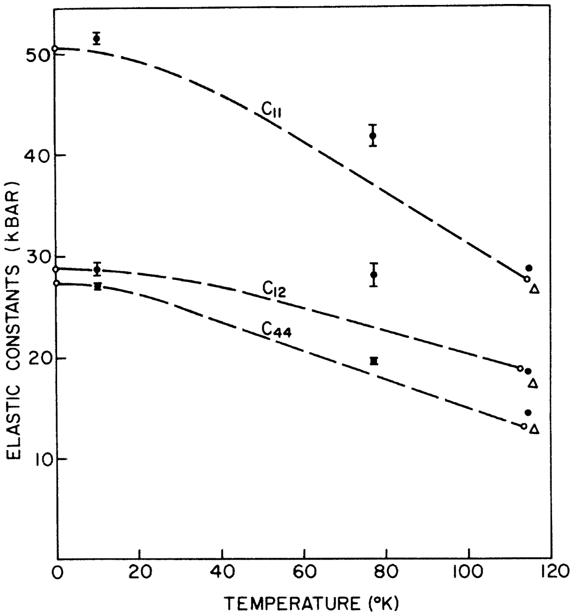

FIG. 4. Elastic constants of krypton as a function of temperature. Calculated values (○) of Barker *et al.* (Ref. 27) at 0 K, and of Klein and Murphy (Ref. 29) at 115 K. Experimental values: (●) neutron-scattering results of Skalyo *et al.* (Ref. 25) at 10 K, of Peter *et al.* (Ref. 20) at 77 K, and of Skalyo and Endoh (Ref. 5) at 114 K; (△) present Brillouin-scattering results at 115.6 K. (The dashed curves serve merely as guides.)

modulus is ~6% higher than the x-ray value of Urvas *et al.*[16] and that of Korpiun and Coufal,[14] although at 10 K there should be no difference. Thus, the measurements at 10 and 77 K seem to indicate a large discrepancy between neutron and static measurements of the bulk moduli, which remains unexplained.

C. Elastic constants: Comparison with theoretical values

While considerable advances have recently been made in calculating many of the properties of the rare-gas solids, the outstanding problem with solid krypton is the inadequacy of the pair potentials available to date. In spite of this shortcoming, several calculations of the elastic constants have been made, and these are compared in Table IV and Fig. 4 with available experimental values.

One of the earliest calculations was by Holt *et al.*,[26] who used the quasiharmonic approximation, with a Lennard-Jones 6-12 potential, and all-neighbor interactions. Their values of the elastic constants at 115 K are not in good agreement with the present experimental values.

Barker *et al.*[27] have made a perturbation-theory calculation of the elastic constants and dispersion curves at 0 K, using an analytic form for the krypton pair potential proposed by Barker and Pompe.[28] Their values are in surprisingly good agreement with the 10 K neutron scattering results of Skalyo *et al.*[25] This same potential was used by Klein and Murphy[29] in a Monte Carlo computer calculation of the elastic constants at 115 K. They also included three-body interactions described by the Axilrod-Teller-Muto[30] (ATM) potential which gave contributions of 3.6(15%), 2.2(12%), and 0.7(6%) kbar to C_{11}, C_{12}, and C_{44}, respectively. As shown in Table IV, the results of Klein and Murphy[29] are in rough agreement with the present values; the agreement with C_{44} is good, but discrepancies of 3% in C_{11} and 8% in C_{12} are apparent. These are due in part to the inadequacy of the pair potential, and to the possible contribution of many-body forces of higher order than that given by the three-body ATM potential.

The experimental and calculated values of the anisotropy parameter A are in reasonably good agreement both at low and high temperatures. The value of ~2.7 near the triple point of krypton is the same for solid xenon,[1] argon,[3] and neon[4] near their triple points.

To date, the calculated values of the elastic constants given by Klein and Murphy[29] are the best available for comparison with the present Brillouin-scattering results. However, there have been recent reports[31,32] of refinements in the pair potential for krypton. Once the pair potential has been established, it will be possible to use the present values of the elastic constants to obtain information of nonadditive exchange forces or higher-order many-body forces in krypton.

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[†] Present address: Dept. of Physics, Imperial College of Technology, London, England. Holder of National Council of Canada "1967 Science" Scholarship, Univ. of Toronto 1973–74.

[‡] Present address: Dept. of Physics, University of Cincinnati, Cincinnati, Ohio 45221. Post-doctorate Fellow 1971–73.

[§] Present address: Dept. of Astronomy, University of Toronto, Toronto, Canada, M5S1A7. Holder of a National Research Council of Canada scholarship, 1970–72 and of the Kodak of Canada Fellowship, 1972–73.

[1] W. S. Gornall and B. P. Stoicheff, Phys. Rev. B 4, 4518 (1971).

[2] S. Gewurtz, H. Kiefte, D. Landheer, R. A. McLaren, and B. P. Stoicheff, Phys. Rev. Lett. 29, 1768 (1972).

[3] S. Gewurtz and B. P. Stoicheff, Phys. Rev. B 10, 3487 (1974).

[4] R. A. McLaren, H. Kiefte, D. Landheer, and B. P. Stoicheff, Phys. Rev. B 11, 1705 (1975).

[5] J. Skalyo, Jr. and Y. Endoh, Phys. Rev. B 7, 4670 (1973).

[6] H. E. Jackson, D. Landheer, and B. P. Stoicheff, Phys. Rev. Lett. 31, 296 (1973).

[7] A. C. Sinnock and B. L. Smith, Phys. Rev. 181, 1297 (1969).

[8] P. Korpiun and H. J. Coufal, Phys. Status Solidi A 6, 187 (1971).

[9] In Eq. (19) of Ref. 1, p_{44} should be replaced by $2p_{44}$.

[10] N. R. Werthamer, Phys. Rev. B 6, 4075 (1972).

[11] D. S. Kupperman and R. O. Simmons, J. Phys. C 4, L5 (1971).

[12] P. A. Bezuglyi, L. M. Tarasenko, and O. I. Baryshevskii, Sov. Phys. Solid State 13, 2003 (1972).

[13] P. Korpiun, A. Burmeister, and E. Lüscher, J. Phys. Chem. Solids 33, 1411 (1972).

[14] P. Korpiun and H. J. Coufal, Phys. Status Solidi A 6, 187 (1971).

[15] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. Lond. 78, 1462 (1961).

[16] A. O. Urvas, D. L. Losee, and R. O. Simmons, J. Phys. Chem. Solids 28, 2269 (1967).

[17] D. L. Losee and R. O. Simmons, Phys. Rev. 172, 944 (1968); W. Schonknecht, Ph.D. thesis (University of Illinois, Urbana-Champaign, 1971) (unpublished).

[18] M. Pistorius, Z. Angew. Phys. 29, 145 (1970).

[19] W. B. Daniels, G. Shirane, B. C. Frazer, H. Umbeyashi, and J. A. Leake, Phys. Rev. Lett. 18, 548 (1967).

[20] H. Peter, J. Skalyo, Jr., H. Grimm, E. Lüscher, and P. Korpiun, J. Phys. Chem. Solids, 34, 255 (1973).

[21] R. A. Cowley, Proc. Phys. Soc. Lond. 90, 1127 (1967).

[22] E. C. Svensson and W. J. L. Buyers, Phys. Rev. 165, 1063 (1968); J. S. Blinick and H. J. Maris, Phys. Rev. B 2, 2139 (1970).

[23] G. Niklasson, Phys. Kondens. Mater. 14, 138 (1972).

[24] V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. B 4, 567 (1971).

[25] J. Skalyo, Jr., Y. Endoh, and G. Shirane, Phys. Rev. B 9, 1797 (1974).

[26] A. C. Holt, W. G. Hoover, S. G. Gray, and D. R. Shortle, Physica (Utr.) 49, 61 (1970).

[27] J. A. Barker, M. V. Bobetic, and M. L. Klein, Phys. Lett. A 34, 415 (1971).

[28] J. A. Barker and A. Pompe, Aust. J. Chem. 21, 1683 (1968).

[29] M. L. Klein and R. D. Murphy, Phys. Rev. B 6, 2433 (1972).

[30] B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943); Y. Muto, J. Phys. Soc. Jpn. 17, 692 (1943); B. M. Axilrod, J. Chem. Phys. 17, 1349 (1946); 19, 719 (1951); 19, 724 (1951).

[31] K. K. Docken and T. P. Schafer, J. Mol. Spectrosc. 46, 454 (1973).

[32] U. Buck, M. G. Dondi, U. Valbusa, M. L. Klein, and G. Scoles, Phys. Rev. A 8, 2409 (1973).