Lattice Dynamics with Three-Body Forces. II. Krypton

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An accurate pair potential for interaction of krypton atoms is derived by methods similar to those previously used for argon. This potential, in conjunction with the Axilrod-Teller three-body interaction, is used to calculate the Debye parameter, thermal expansion, and bulk modulus for crystalline krypton at low temperatures $[(0-12)^{\circ}K]$. Agreement with experiment is very good except for a discrepancy of about 4% in the bulk modulus. As in the case of argon, this is tentatively ascribed to the effect of the helium pressure fluid on the lattice spacing.

I. INTRODUCTION

Following the successful construction of a realistic potential function for argon,¹ we now describe similar calculations for krypton. We have used the analytic form for the pair potential first proposed by Barker and Pompe² and subsequently used by Bobetic and Barker¹:

$$u(R) = \epsilon \left(e^{\alpha (1-r)} \sum_{i=0}^{L} A_i (r-1)^i - \sum_{i=0}^{2} \frac{C_{2i+6}}{\delta + r^{2i+6}} \right), \quad (1)$$

where $r = R/R_m$, with R_m being the separation at the minimum of the potential, and ϵ the depth at the minimum.

Here also we use the basic approximations of Refs. 1 and 2, namely, we assume that the potential energy of a set of inert-gas atoms can be written in the form

$$U = \sum_{i < j} u^{(2)}(ij) + \sum_{i < j < k} u^{(3)}(ijk) + \cdots, \qquad (2)$$

in which we neglect terms beyond the triplet term, and for the triplet term $u^{(3)}(ijk)$ we use the long-range Axilrod-Teller form

$$u^{(3)}(ijk) = \nu (1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3) / (R_1 R_2 R_3)^3.$$
 (3)

For the coefficient ν we adopt the value 220.4 $\times 10^{-84}$ erg cm⁹ due to Leonard³; this is close to the value given by Bell and Kingston.⁴

The solid-state calculations were made by the same methods used for argon and described in Refs. 1 and 2. In calculating the anharmonic corrections, we again neglected non-nearest-neighbor and three-body interactions.

II. POTENTIAL FOR KRYPTON

To determine the potential function for krypton

we used Eq. (1) with L = 5. We first attempted to follow exactly the procedure of Ref. 1, in which the potential function was constrained to agree with high-energy molecular-beam scattering results, experimental second-virial coefficients, the known long-range dispersion coefficients, the experimental value of the Debye temperature at 0 °K, and the experimental lattice spacing and cohesive energy of crystalline krypton at 0 °K.

For experimental second-virial coefficients we used the measurements of Weir *et al.*, ⁵ Trappeniers *et al.*, ⁶ and Whalley and Schneider. ⁷ For the nearest-neighbor distance and cohesive energy of solid krypton at 0 °K, we adopted the values 3.9922 Å and -2666 ± 7 cal/mole given by Horton. ⁸

From the high-energy molecular-beam data of Amdur and Mason, ⁹ we adopted the values u(r)/k= 7233 °K, $d\ln u(R)/dR = -1.95$ Å⁻¹ at R = 2.78 Å. For the long-range coefficients of R^{-6} , R^{-8} , and R^{-10} we adopted the values -122.43×10^{-60} erg cm⁶,

TABLE I. Potential for krypton.

<i>€ / k</i> (°K)	197.431
$R_0(\text{\AA})$	3.5944
$R_m(\text{\AA})$	4.0152
A_0	0.247948
A_1	-4.458549
A_2	- 13.68881
A_3	- 57.824025
A_4	-242.091916
A_5	-337.0
	1.074658
	0.171450
C_{10}	0.014319
α	13,5
δ	. 0.01

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FIG. 1. Comparison of present potential (solid curve) with 6:12 potential with parameters due to Sherwood and Prausnitz (Ref. 14).

- $315 \times 10^{-76} \text{ erg cm}^8$, and - $423 \times 10^{-92} \text{ erg cm}^{10}$. The value of C_6 is that of Leonard, ³ while the values of C_8 and C_{10} are calculated using the approximate values of Margenau¹⁰ for the ratios C_8/C_6 and C_{10}/C_6 together with this value of C_6 .

The parameter α was tentatively varied from 13 to 21 to attempt to reproduce both the experimental Debye parameter and the compressibility at 0 °K. We chose as a best estimate $\alpha = 18$ for which inverse interpolation gave $R_0 = 3.6184$ Å while the bulk modulus was 3.56×10^{10} dyn cm⁻². This value of the bulk modulus is 3.4% higher than the experimental value of Urvas *et al.*¹¹ Smaller values of α gave higher values of the bulk modulus, and for larger values of α no solutions of the simultaneous equations determining the parameters were found.

Examination of the results of the calculations of solid-state properties using this potential with $\alpha = 18$ showed much larger corrections for anharmonicity than were found for argon. Since this appeared unlikely, we calculated viscosities for gaseous krypton, finding discrepancies of about 4% from the measurements of Dawe and Smith¹² at high temperatures. A communication from Mason¹³ indicated that because of experimental difficulties



FIG. 2. Difference between experimental and calculated second-virial coefficients; experimental data of Weir *et al.* (Ref. 5): \circ ; Trappeniers *et al.* (Ref. 6): \Box ; Whalley and Schneider (Ref. 7): \bullet .



FIG. 3. Percentage difference between experimental and calculated viscosities; experimental data of Dawe and Smith (Ref. 12): •; Clarke and Smith (Ref. 15): □.

the logarithmic slope of the potential for krypton derived from his measurements is less precisely known than the corresponding number for argon and should be regarded as uncertain. Accordingly, we decided to use this as another adjustable parameter, seeking the value which gave best agreement with the viscosities. The resulting value for the logarithmic slope at 2.78 Å was $-3.5 Å^{-1}$. With this value and following otherwise the procedure described in Ref. 1 for argon, we found the parameters for the potential function for krypton listed in Table I. In Fig. 1 we compare the present potential with a Lennard-Jones 6:12 potential with parameters $\epsilon/k = 164 \,^{\circ}$ K, $\sigma = 3.827 Å$ as determined by Sherwood and Prausnitz.¹⁴

III. RESULTS

In Fig. 2 we show (by means of a deviation plot) a comparison of calculated and experimental second-virial coefficients. Agreement is excellent. Figure 3 makes a similar comparison for gas viscosities. The agreement is excellent at higher temperatures (as expected) and good at low temperatures. Calculated and experimental thermal diffusion ratios are shown in Fig. 4. The most recent measurements, those of Paul and Watson,¹⁹



FIG. 4. Thermal diffusion ratio R_T . Solid curve, calculated values; experimental data of Corbett and Watson (Ref. 16): \times ; Moran and Watson (Ref. 17): \Box ; Moran and Watson (Ref. 18): \triangle ; Paul and Watson (Ref. 19): c.



FIG. 5. Calculated (solid curve) and experimental (Ref. 20) (circles) Debye parameters.

are close to the calculated curve.

For the nearest-neighbor distance and cohesive energy at 0°K, we found 3.9921 Å and -2667.9cal/mole, compared with the experimental values 3.9922 Å, -2666 ± 7 cal/mole. This of course is simply a measure of the accuracy of our fitting procedure.

In Fig. 5 the calculated Debye parameters Θ_D are compared with the experimental data of Finegold and Phillips.²⁰ Considering that the specific heat data at nonzero temperatures were not used in determining the potential the agreement is good. The deviations in the range (8-12) °K may be partly attributable to error in the perturbative calculation



FIG. 6. Integrated thermal expansion d(T) - d(0) (in Å); solid curve calculated; experimental data of Tilford and Swenson (Ref. 21): •; experimental data of Losee and Simmons (Ref. 22): I.



FIG. 7. Differential collision cross-sections (Ref. 23) intensities for krypton (upper curve) and argon.

of anharmonicity.

In Fig. 6 we show calculated and experimental values of the integrated thermal expansion d(T)-d(0), where d is the nearest-neighbor distance. The expansivity data of Tilford and Swenson²¹ were integrated using Simpson's rule. As a check, a seven-point integration formula gave negligible differences from the Simpson's-rule results. In the same figure comparison is made with the xray lattice-parameter measurements of Losee and Simmons.²² The calculated results agree better with the x-ray data than with the results of Tilford and Swenson, although the latter are probably more accurate. This may indicate that the third derivative of our potential near the minimum is a little too negative (i.e., numerically too large). If this derivative were reduced in magnitude by about 8%, it would bring our results into agreement with those

TABLE II. Bulk modulus v dp/dv (10¹⁰ dyn cm⁻²).

<i>T</i> (°K)	v dp/dv		
0.30	3.6003		
2.08	3.6002		
4.16	3.5993		
4.76	3,5985		
5.95	3,5959		
8.33	3.5845		
10.11	3.5700		
12.49	3.5430		

TABLE III.	Contributions	to	energy.
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d(0) (Å) (calc.)	U_{2b} (cal/mole)	U_{3b} (cal/mole)	<i>U_z</i> (cal/mole)	U _{tot} (cal/mole)
3,992 09	- 3051.53	+236.53	+146.84	-2667.86

of Tilford and Swenson. This is in qualitative and even roughly quantitative agreement with conclusions that can be drawn from molecular beam differential scattering measurements of Cavallini et al.²³ which became available to us after the present work was completed. These results are shown in Fig. 7. From these data Cavallini et al.²³ estimated R du(R)/dR at the inflexion point of the potential to be 660 °K, whereas our potential gives 598 °K. Since this quantity is roughly inversely proportional to the third derivative, these differences are consistent with the evidence of the thermal expansion.

The discrepancies for krypton in Fig. 7 are similar to, but somewhat larger than, those for argon. In the case of argon a small change of the potential led²⁴ to excellent agreement both with the molecular-beam data and with liquid-state pressures. There is every reason to believe that a similar small change would make our krypton potential consistent with all the facts, but this requires further investigation.

In Table II we show calculated values of the bulk modulus. Its value at 4.25 $^{\circ}$ K is 3.599 \times 10¹⁰ dyn cm^{-2} , and this is about 4.6% higher than the experimental value of 3. 44×10^{10} dyn cm⁻² due to Urvas et al.¹¹ This discrepancy is in the same sense as, but only about half as large as, the corresponding

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discrepancy which we found for the case of argon. We suggested that the discrepancy for argon was due to the effect of the helium used as pressure fluid on the lattice spacing. The present result lends some weight to that suggestion, since the observed irreversible effect of helium on the lattice spacing in krypton (7 ppm) was a little less than half that in argon (17 ppm).

Phonon dispersion curves calculated with the present potential have already been published, ²⁵ and are in good agreement with available experimental evidence.

To give some feeling for the magnitude of various effects in crystalline krypton we list in Table III the separate two-body and three-body contributions to the static lattice energy, as well as the vibrational zero-point energy.

Rowlinson et al.^{26,27} have discussed three-body interactions in terms of their contributions to an "effective pair potential" which depends on temperature and density. In the case of argon, Barker et al.²⁸ found that these contributions accounted for only a small part of the difference between the 6:12 potential and the actual potential. The major difference is due to the incorrect shape of the 6:12 curve; the long-range coefficient of R^{-6} is too large by a factor of about 2, and this must be compensated by a reduction in the depth at the minimum. Similar conclusions are valid in the case of krypton.

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Deformation Potentials for Excitons in Cuprous Halides[†]

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The hydrostatic-pressure shifts of the $Z_{1,2}$ and Z_3 exciton peaks were measured in thin films of cubic CuCl, CuBr, and CuI at 90 K. That of the E_1 peak in CuI also was measured. The deformation potentials of all Z excitons and of the E_1 excito. in CuI, about -1 eV, are more than twice those of the Z excitons in CuCl and CuBr. This suggests the two valence bands in CuI may be considerably more mixed than in CuCl and CuBr.

I. INTRODUCTION

The cuprous halides, CuCl, CuBr, and CuI, are insulators whose band structures have been considered to be related to those of the group-IV, -III-V, and -II-VI cubic semiconductors, when account is taken of the increased ionicity.^{1,2} They are cubic (zinc-blende structure) below about 640 K.³⁻⁵ Cardona² measured the absorption spectra of these compounds and found two sharp peaks at low energy and a stronger peak at higher energy. Up to that time, it was believed that the valence band was largely composed of halogen-p-like functions. The splitting of the two lowest-energy peaks was interpreted as a spin-orbit splitting, since it increased from chloride to bromide to iodide, but because it was smaller than the spin-orbit splitting of the halogen, an appreciable Cu-3d component was believed to be present in the valence band. The positions of the band edges could not be reconciled with predictions from the gaps in III-V and II-VI compounds.²

Song^{6, 7} calculated energy bands for CuCl. He found that there were two valence bands, with a gap of about 2 eV between them (Fig. 1). At the center of the zone, the uppermost band is derived primarily from Cu⁺-3*d* levels (~80% of the charge density for the Γ_{15} state) while the lower is predominantly from Cl⁻-3*p* levels (~80% for the lower Γ_{15}). He showed that only the lower band was to be associated with the valence band in cubic semiconductors, and its position could be extrapolated with reasonable accuracy from band gaps in cubic semiconductors. The exciton spectrum of CuCl consists of a sharp line called the Z_3 line, followed at higher energy by the $Z_{1,2}$ line, which often is split into two by strain.⁸ According to Song⁷ these originate from the spin-orbit-split Γ_{15} levels, Γ_7 and Γ_8 , respectively, both in the upper valence band (Fig. 1). The lower valence band gives a series of absorption structures, beginning with a peak called E_1 and extending into the vacuum ultraviolet.² The E_1 peak originates at the lower Γ_{15} level and corresponds to the lowest-energy direct exciton at Γ in the group-IV, -III-V, and -II-VI semiconductors.

The E_1 peak is stronger than the $Z_{1,2}$ and Z_3 peaks, and is "allowed," while the $Z_{1,2}$ and Z_3 peaks correspond roughly to dipole-forbidden atomic transitions, $Cu^+ 3d \rightarrow Cu^+ 4s$, that are allowed at \vec{k} = 0 by the admixture of $Cl^{-}3p$ wave functions. CuBr presumably has a similar set of valence bands, and so might CuI, but in both of these, the $Z_{1,2}$ line is at lower energy than the Z_3 line,² indicating a reversal of sign of the spin-orbit parameter. The gap between the lower and upper valence bands may diminish in CuBr and CuI. (The $Z_{1,2} - E_1$ separations diminish.) The two valence bands then would become more mixed in atomic-wave-function character. (In AgCl, the Cl⁻ 3p and Ag⁺ 4d states completely mix, except at a few points, into one complicated valence band.^{9,10}) Extensive mixing should make the $Z_{1,2}$ and Z_3 absorption peaks stronger with respect to the E_1 peak, but this does not seem to be the case.²

Measurements of the hydrostatic-pressure coefficient of band gaps have shown that, within a group of materials of identical crystal structure and simi-