Relationship between Adiabatic Elastic Constants and the Slopes of Phonon Dispersion Curves for Rare-Gas Solids*

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The velocity of first sound is calculated from the adiabatic elastic constants using the lowest-order self-consistent phonon scheme. The velocity of sound is also calculated from the limiting slopes of phonon dispersion curves using a conserving approximation. Results are presented for models appropriate to solid Kr and solid Xe. The maximum difference appears to be of order 4% or less at the respective melting temperatures. This has the important consequence that the limiting slopes of phonon dispersion curves should be in agreement at least to this accuracy with conventional ultrasonic measurements and Brillouin-scattering experiments. Thus the apparent discrepancies between ultrasonic and neutron data in solid Ar do not appear to be due to this effect.

I. INTRODUCTION

Phonon energies have now been measured[1-5] in several rare-gas solids (RGS), and the velocity of sound has been observed by conventional ultrasonic methods,[6-10] Brillouin scattering,[11] and stimulated Brillouin scattering.[12] Further experiments will no doubt be forthcoming. At present for solid fcc Ar there are discrepancies between the ultrasonic work and the slopes of phonon dispersion curves.[4] These differences probably have their origin in the difficulty associated with carrying out experiments on RGS. In this connection a possible large difference between the velocities of zero sound and first sound could also be considered. Such an effect has already been predicted[13] and observed[14] in alkali halide crystals and in quartz.[15] It is the purpose of this paper to give an estimate for the magnitude of this effect in RGS. Previous estimates for RGS have been vague and only qualitative in nature. Accordingly we calculate here the adiabatic elastic constants (which determine the velocity of first sound) and compare these with elastic constants derived from the appropriate slopes of phonon dispersion curves. In spirit the calculations follow closely the work of Cowely on alkali halides.[13] The range of validity of the conventional perturbation theory of anharmonic effects seems to be considerably wider for alkali halides than RGS.[16] Thus for RGS it is necessary to use the self-consistent phonon theory if the calculated high-temperature properties are to be at all meaningful.[17] Some care is needed to ensure that a conserving approximation is employed when calculating these sound velocities within a self-consistent phonon scheme.[18,19] Section II outlines our calculations and presents the results for Lennard-Jones (12-6) nearest-neighbor models appropriate to Kr and Xe. Anticipating these we find the difference between the neutron velocity of sound and first sound to be always less than 4%. Therefore the discrepancies alluded to above would appear to be due to experimental difficulties rather than any intrinsic property of a perfect fcc RGS.

II. OUTLINE OF CALCULATIONS AND RESULTS

The theory of self-consistent elastic constants has been given in detail elsewhere.[18,20] Cowley's article[13] gives an excellent discussion of why the propagation of first sound is determined by the adiabatic elastic constants, and we shall not repeat his arguments here. Our calculation of isothermal elastic constants follows exactly the procedures outlined in Ref. 20. Adiabatic (first-sound) elastic constants were then obtained by thermodynamic correction in the usual fashion. The interatomic potentials were the same as those used previously.[17,20] Some selected results for Kr and Xe are shown in Table I. We recall that for cubic crystals the elastic constants are usually obtained from the wave propagation directions using the following relationships:

$$[\xi 00]L \rightarrow C_{11},$$

TABLE I. Comparison of C^S, adiabatic (first-sound) elastic constants, with C^0, the elastic constants obtained from the slopes of phonon dispersion curves.

Substance (lattice constant)	Temperature (°K)	Pressure (kbar)	Direction	ξ	C^0 (kbar)	C^s (kbar)
Kr (5.67 Å)	2.5	−0.38	$[00\xi]T$	0.030	22.59	22.61
			$[00\xi]T$	0.100	22.43	22.61
			$[0\xi\xi]T_1$	0.167	22.02	22.61
			$[00\xi]L$	0.030	44.53	44.58
			$[00\xi]L$	0.100	44.23	44.58
			$[0\xi\xi]T_2$	0.167	11.37	11.66
	91	1.25	$[00\xi]T$	0.100	22.93	22.23
			$[0\xi\xi]T_1$	0.167	22.69	22.23
			$[0\xi\xi]T_2$	0.167	11.59	11.18
	186	3.07	$[00\xi]T$	0.100	24.21	23.26
			$[0\xi\xi]T_1$	0.167	24.18	23.26
			$[0\xi\xi]T_2$	0.167	12.02	11.12
Xe (6.354 Å)	160	−0.22	$[00\xi]T$	0.030	15.03	14.32
			$[00\xi]T$	0.100	15.08	14.32
			$[0\xi\xi]T_1$	0.020	15.13	14.32
			$[0\xi\xi]T_1$	0.070	15.08	14.32
			$[00\xi]L$	0.030	33.91	32.13
			$[00\xi]L$	0.100	33.87	32.13
			$[0\xi\xi]T_2$	0.020	8.48	8.01
			$[0\xi\xi]T_2$	0.070	8.60	8.01
			$[0\xi\xi]L$	0.070	40.09	38.42

$$[\xi 00]T \to C_{44},$$

$$[\xi\xi 0]T_1 \to C_{44},$$

$$[\xi\xi 0]T_2 \to \tfrac{1}{2}(C_{11} - C_{12}), \quad \text{etc.}$$

Wallace[21] has discussed the generalization to the case of nonzero initial stress. In actual numerical calculations for RGS this latter effect is important. Elastic constants obtained from the slopes of the phonon branches indicated above[22] are also shown in the table. The appropriate phonon energies were calculated using the theory outlined in Ref. 19 and identical numerical procedures. We stress that our phonon energies and the elastic constants have been calculated using a conserving approximation.[18]

At low temperatures and small wave vector the elastic constants are in excellent agreement as they should be[13] which incidentally confirms our numerical work. The difference between the neutron sound velocity and first sound increases as the temperature rises but is never more than a few percent. The agreement to better than 1% between neutron elastic constants derived from $[\xi 00]T$ and $[\xi\xi 0]T_1$ phonon branches of Xe at 160 °K, seems to indicate that for RGS, unlike alkali halides,[13] the usual symmetry properties[21] hold very well. Moreover, if the models employed here are at all realistic, and they are believed to be, then it will be extremely difficult to detect any differences between zero and first sound experimentally in RGS.

III. SUMMARY

Using a simple nearest-neighbor model for the interatomic forces and a self-consistent phonon theory for the dynamics, we have calculated the difference between the velocity of first sound and that derived from the slopes of phonon curves in RGS, Kr, and Xe. We find the difference between the respective sound velocities to be always less than a few percent.

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[22]The wave velocities were obtained from the phonon curves by computing phonon energies and dividing by the wave vector. Thus dispersion has some effect as can be seen from the ξ dependence of the Kr 2.5 °K results. However, dispersion causes $C^S > C^O$ which therefore tends to reduce the effect discussed in this paper.

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Theory of Resonant Raman Scattering in Crystals: A Generalized Bare-Exciton Approach*

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The bare-exciton theory of light scattering in crystals is generalized to include dispersive effects, and to incorporate damping in a first-principles calculation. The theory is applied to exciton-mediated Raman scattering; expressions for the first- and second-order Raman cross sections due to a single discrete exciton level are derived, and the resonance behavior investigated. For small couplings and intermediate dampings the predictions of the present generalized theory are very similar to available bare-exciton and undamped-polariton predictions, while differing, however, for large couplings. The cross sections are resonant when the incoming or outgoing photon frequencies lie near an exciton frequency, and peak sharply for small photon-exciton couplings and dampings. Actual calculations are presented for various choices of the parameters, among them parameters appropriate to CdS. A comparison of the present theory with other theories and with experiment is carried out.

I. INTRODUCTION: HAMILTONIAN, BACKGROUND EFFECTS, AND GENERAL CONSIDERATIONS

A. Introductory Remarks

Encouraged by recent advances in laser technology, Raman scattering (RS) from crystals at optical frequencies has emerged as a useful tool for studying the electronic, as well as the lattice, properties of crystals.[1] A fundamental class of electronic excitations in a large variety of crystals (including ionic, molecular, and semiconducting ones) are interacting electron-hole pairs, or excitons. RS enables an investigation of exciton energy levels and the nature of their interactions with light and lattice vibrations.[2]

A number of papers have employed, in various forms, a "bare-exciton," or perturbation-theory, approach[3] to light-scattering problems, which has the advantages of being relatively simple and intuitively appealing. Toyozowa's treatment of light absorption,[4] and Ganguly and Birman's (GB) treatment[2] of RS, provide examples of the application of this approximate procedure. Its major advantage, as will be seen later, lies in enabling a fairly straightforward analysis of certain of the seemingly more complex aspects of a given problem. We will develop the bare-exciton framework here because we believe it leads to a useful approximate theory of resonance RS, in a form which may be followed by experimentalists and nonexperts in the field. In this situation, we feel, its full exposition and exploitation constitutes a highly desirable adjunct to the development and implementation of more rigorous and more elegant approaches.

An example of a more elegant (and, from a *computational* point of view, much more complicated) approach to light-scattering problems is that of polariton (composite-quasiparticle) theory.[5-7] We have, e.g., applied polariton theory to certain aspects of RS in insulators, in a parallel paper.[6] The purpose of the present work, on the other hand, is (a) the generalization of the bare-exciton framework in a number of ways especially relevant for calculations of resonance phenomena; (b) a detailed application of the theory to first- and second-order RS in insulators in the optical frequency regime.

The results of the present approach, which will, from here on, be referred to as "generalized-exciton theory," will be contrasted with those of polariton theory[6,7] for certain special cases.

The present generalizations include:

(a) A derivation of a formalism which accounts for background effects, including, as well, the presence of background absorption. This is important in reducing the complexity of various calculations by allowing one to concentrate on a limited number of interactions of interest (cf. Secs. II B and II C).

(b) An introduction of scattering theory so as to include damping effects from first principles. Such a procedure is essential in the resonance regime, where, if damping were omitted, the resonances would appear as singularities in the cross section,[2] thus limiting the usefulness of the results (cf. Sec. II A and Appendix).

(c) A proposal of an empirically introduced, but physically motivated, procedure to account for dispersion of light near resonance, which may be shown to lead to results in agreement with more ex-