Phonons in Rare-Gas Solids Close to Melting

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(Received 24 November 1986)

Calculations of the phonon spectrum of argon with use of a realistic potential, and with the inclusion of short-range correlation effects by means of the Horner *Ansatz*, are in excellent agreement with recent neutron-scattering experiments, even within 3 K of the melting temperature. The elastic constants and heat capacity C_p are also in good agreement. The method also gives results for a model of xenon at 163.9 K which agree well with values obtained with use of the Monte Carlo method.

PACS numbers: 63.20.Dj, 61.55.Dc, 62.20.Dc, 65.40.Em

The theory of lattice dynamics has been formulated for some time.[1] But it is well known that a detailed application of theoretical results to the experiments, especially near melting, runs into formidable problems. This is particularly true for rare-gas solids (RGS), where there are strong anharmonicities and the need for short-range correlations due to the hard core in the interatomic potential. A way to cope with these problems is to introduce computer simulation techniques, but these, though exact in principle, are often still of low numerical accuracy, particularly molecular-dynamics results for $S(\mathbf{Q},\omega)$, and they do not apply at low temperatures.

We argue that a reliable quantitative examination of the contents of lattice dynamics applied to RGS over the whole available temperature range is long overdue. Only in this way can we be sure of the validity of the practical approximation needed to make the theoretical expressions tractable and hence of the usefulness of the underlying physical ideas. There is clearly great intellectual satisfaction in being able to show that a single formulation of lattice dynamics can span the entire range of existence of these solids.

Recently, Eckert and Youngblood[2] have made new detailed measurements of the phonon frequencies and line shapes in argon at 81 K. It is the purpose of this Letter to show that their measured dispersion curves are excellently described by a lattice-dynamical theory which includes short-range correlation effects within the Horner *Ansatz*.[1] In addition, we make some comparisons with Monte Carlo results for a nearest-neighbor Lennard-Jones model of xenon, again at a temperature very close to melting. The self-consistent harmonic approximation (SCH) with anharmonic perturbation theory has been used by Glyde and Smoes[3] in calculation of $S(\mathbf{Q},\omega)$ in argon. The Horner formalism goes beyond this work in three respects: (1) The pair correlation function is modified from its SCH form g_h by factors to give the correct behavior at short distances while preserving the normalization, peak positions, and second moment. For a neighbor at site $\mathbf{R}_p$

$$g(\mathbf{R}_p,\mathbf{r}) = g_h(\mathbf{R}_p,\mathbf{r})\exp\{-\beta\phi(r)\}\sum_{i=0}^{2} a_i(r-R_p)^i.$$

(2) It is assumed that the averaged potential well in which a pair of atoms moves has time to relax as the atoms move. $g(\mathbf{R}_p,\mathbf{r})$ thus depends on the instantaneous value of $\mathbf{R}_p$, and the force constants $M_{\alpha\beta}$ contain contributions arising from the variation of the coefficients a_i with R_p:

$$M_{\alpha\beta} = -\sum_{i=0}^{2}\int \exp\{-\beta\phi(r)\}(r-R_p)^i[a_i\nabla_\beta g_h\nabla_\alpha\phi(r) - (\partial a_i/\partial R_{p\beta})g_h\nabla_\alpha\phi(r)]d^3r.$$

(3) The cubic shifts to the phonon energies are included self-consistently. That is, the intermediate phonon energies used in the calculation of the cubic shifts themselves include the shifts. While this may seem plausible, it should be noted that there are many other corrections to the phonon self-energies, which are of the same order, that are being omitted. Numerical cancellation has played an important role in the subject, and so the test of the Horner *Ansatz* lies in the results.

We have applied the formalism to a realistic model of ^{36}Ar. The quadratic force constants were calculated for eight shells of neighbors with use of the two-body potential of Aziz and Chen,[4] supplemented by the three-body Axilrod-Teller-Muto potential.[5] The force constants for the second- and third-neighbor shells were smeared in the SCH approximation, while for the nearest neighbors we used the full Horner *Ansatz* The cubic matrix elements included the contributions from the first three shells of neighbors. In order to include the cubic shifts self-consistently, the shifts were calculated for 27 phonons at 12 wave vectors and a set of corrections to the

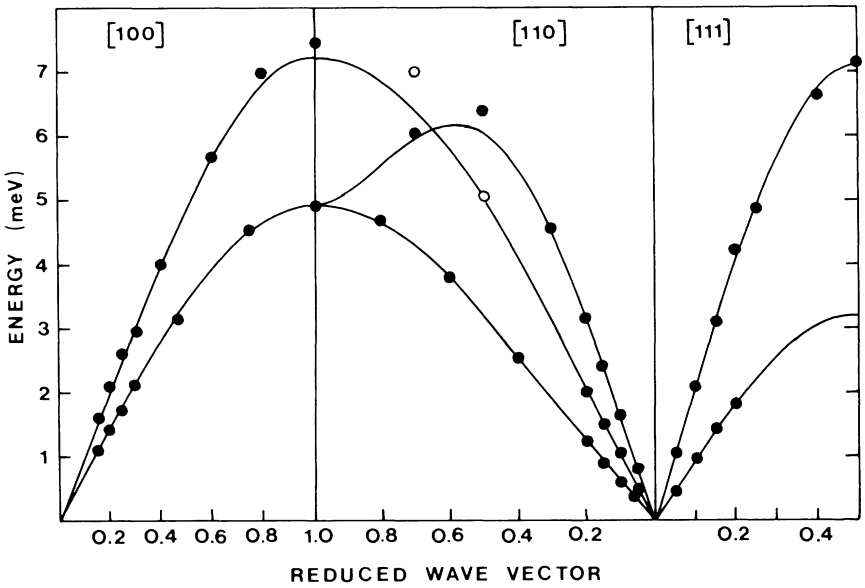

FIG. 1. Phonon dispersion relations in ^{36}Ar at 81 K. Points are the neutron-scattering results of Eckert and Youngblood. Lines are the present calculation.

quadratic force constants for the first three shells of neighbors were fitted to them. These corrections were then applied in succeeding iterations of the SCH equations. Typically, eight iterations of the SCH equations were performed before the cubic shifts were recalculated.

The phonon dispersion curves at 81 K, calculated from the fitted force constants, are shown in Fig. 1. With the exception of three points the agreement is excellent. The zone-boundary longitudinal peak is extremely broad, and the error estimate of Eckert and Youngblood encompasses our value. The discrepancy is probably due to the two-phonon contribution to $S(Q,\omega)$, which Glyde and Smoes[3] have shown to give rise to a high-energy shoulder. The experimental points shown as hollow circles were obtained serendipitously under conditions where they should normally be invisible and are more uncertain than the other values. The remaining discrepant point, in the [110] direction, also seems to appear slightly high in calculations at low temperatures,[3] and may indicate a small shortcoming of the interatomic potential. Bearing these comments in mind, we can claim that the agreement which we obtain at a temperature within 3 K of the melting point is as good as the agreement which can be obtained at 10 K and we view this result with great satisfaction.

It is also possible to extract values of the zero-sound elastic constants from the slopes of the dispersion curves at long wavelengths, using either curves measured by inelastic neutron scattering, or the calculated spectral functions. Experimental measurements of the long-wavelength modes were performed by Fujii *et al.*[6] at a temperature of 82 K and the elastic constants they obtained are given in Table I together with our calculated values. The dispersion curves calculated for 82 K are in excellent overall agreement with the measurements and the small differences between the two steps of elastic constants are probably entirely due to different procedures for getting the elastic constants from the dispersion curves. Also shown in the table are values of the first-sound elastic constants measured by Brillouin scattering, by Gewürtz and Stoicheff.[7] The differences, for c_{11} and especially c_{44}, are slightly larger, and outside the experimental uncertainties, and may reflect a difference between zero-sound and first-sound values.

TABLE I. Elastic constants in argon, at 82 K, and xenon, at 163.9 K.

	Elastic constants (10^8 dyn/cm^2)		
	c_{11}	c_{12}	c_{44}
Ar, present theory	257 ± 3	156 ± 5	130 ± 2
Ar, neutron, Ref. 5	248 ± 6	153 ± 5	124 ± 4
Ar, Brillouin, Ref. 6	238 ± 4	156 ± 3	112 ± 3
Xe, present theory	300 ± 4	150 ± 5	134 ± 2
Xe, Monte Carlo, Ref. 7	290 ± 1.5	154 ± 1.5	117 ± 1

To explore this further we have made an additional comparison, with values of the adiabatic constants calculated by the Monte Carlo method for a nearest-neighbor Lennard-Jones solid.[8] The Lennard-Jones parameters were chosen to correspond to xenon, since this should be the most classical RGS, at a temperature of 163.9 K. The results are also shown in the table, and it can be seen that the deviations between the zero-sound and adiabatic constants follow a very similar pattern to the deviations between zero-sound and first-sound values for argon. In particular, the difference in values for c_{44} is consistent.

An additional intriguing application of the frequencies calculated in the Horner formalism is in the evaluation of the thermodynamic quantities. In theories such as improved self-consistent theory, or the Monte Carlo method, a thermodynamic variable such as the heat capacity is not directly expressible as a single sum over normal modes. However, the Horner formalism is designed to generate a set of frequencies which in some sense give the "best" description of the lattice dynamics, and it is worth trying to use them to calculate thermodynamic functions. In particular, we assume that the entropy can be calculated with the use of the formula corresponding to a set of harmonic normal modes, since this is known to work for the SCH and low-order perturbation theories. The most direct comparison with experiment is to calculate the heat capacity at constant pressure, C_p, by evaluating the entropy at a number of closely spaced temperatures, with the use, for each temperature, of the equilibrium lattice spacing for that temperature. In this way we obtain a value for argon at 80 K of 32.06 J/mole K. The experimental value is 33.17 J/mole K,[9] and the difference is well within the range of estimated values for a vacancy contribution. To eliminate this uncertainty, we have again made a comparison with the Lennard-Jones model of xenon at 163.9 K, and with Monte Carlo calculations.[10] In this case, we calculated a value for the heat capacity at constant volume, C_v, of 2.60 times the gas constant R, while the best Monte Carlo value[10] is 2.64 ± 0.015. While the differences seem to be outside the combined uncertainties, the value given by the present method is happily somewhat higher than the value from improved self-consistent theory, 2.57.

Eckert and Youngblood[2] also reported experimental results at 55 K. Our calculated results give agreement with these values comparable to the agreement at 81 K. We note that the lattice spacing reported by Eckert and Youngblood, 5.440 Å, should in fact be 5.386 Å.[11] This suggests to us that the Horner *Ansatz* holds quantitatively to much lower temperatures then its original derivation suggested.

There is one area where the agreement between theory and experiment may be worse. Eckert and Youngblood[1] made detailed measurements of the line shapes of a number of phonons, and compared them with calculations by Glyde and Smoes[3] which included multiphonon and interference terms. We have calculated only the one-phonon term and it does not adequately reproduce the experimental results. In particular, while the extreme broadening of the longitudinal mode at the [100] zone boundary is reproduced, the transverse mode is calculated to be much sharper than is seen experimentally.

Despite these uncertainties, we feel that the frequencies calculated with use of the high-T Horner *Ansatz* for the pair correlation function and for the force constants are the most useful which have been considered to date, and represent an extension of the lattice-dynamical or "phonon" description of a solid up to the melting point. To the extent that short-range correlations as well as long-range anharmonicities are important in the dynamics of solids, our results show clearly the superiority of self-consistent phonon theory including the Horner *Ansatz*. We know that results that are numerically somewhat inferior to ours can be obtained from simpler versions of lattice dynamics, e.g., improved self-consistent type theories.[3] But such theories are plagued by pathological divergencies which the Horner method cures. As we have pointed out earlier,[3] when we omit points (1) and (2) above, but retain (3), we get divergent results.[12] A full account of our work will be published elsewhere.

[1]H. Horner, in *Dynamical Properties of Solids,* edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1.

[2]J. Eckert and R. W. Youngblood, Phys. Rev. B **34**, 2770 (1986).

[3]H. R. Glyde and M. G. Smoes, Phys. Rev. B **22**, 6391 (1980). We have discussed this work elsewhere; see E. R. Cowley, G. K. Horton, and J. G. Leese, in *Proceedings of the Second International Conference on Phonon Physics, Budapest, Hungary, August 1985,* edited by J. Kollar *et al.* (World Scientific, Singapore, 1985).

[4]R. A. Aziz and H. H. Chen, J. Chem. Phys. **67**, 5719 (1977).

[5]For a justification of this procedure, see J. A. Barker, in *Rare Gas Solids* (Academic, London, 1976), Vol. 1, Ch. 4, p. 212.

[6]Y. Fujii, N. A. Lurie, R. Pynn, and G. Shirane, Phys. Rev. B **10**, 3647 (1974).

[7]S. Gewürtz and B. P. Stoicheff, Phys. Rev. B **10**, 3487 (1974).

[8]E. R. Cowley, Phys. Rev. B **28**, 3160 (1983).

[9]P. Korpiun and E. Lüscher, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1977), Vol. 2.

[10]M. A. Day and R. J. Hardy, J. Phys. Chem. Solids **46**, 487 (1985).

[11]J. Eckert, private communication.

[12]L. B. Kanni and G. K. Khorton, Fiz. Nizk. Temp. (Kiev) **1**, 351 (1975) [Sov. J. Low Temp. Phys. (Kiev.) **1**, 739 (1975)].