The E$_{2g}$ phonon and the elastic constant C_{44} in hexagonal van der Waals bonded solids

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Abstract.   A simple relation between the frequency of E$_{2g}$ phonon modes and the elastic constant C_{44}, derived previously for hexagonal-close-packed metals, is found to be reasonably valid for crystals of solid He, H$_2$, D$_2$ and N$_2$ at or near normal pressure. Good agreement at high pressure for n-H$_2$ suggests that the connection between C_{44} and the phonon frequency also holds over a wide compressional range.

1. Introduction

In lattice dynamical studies [1, 2] of hcp metals using a combination of central and angular forces between various sets of neighbours but involving at most two adjacent basal planes, the elastic constant C_{44} and the E$_{2g}$† phonon frequency $\nu(\text{E}_{2g})$ are related by the following relation:

$$\nu(\text{E}_{2g}) = \frac{1}{2\pi}\sqrt{\frac{4\sqrt{3}a^2 C_{44}}{mc}} \tag{1}$$

where a and c are the lattice constants and m is the atomic mass. The relation arises because in a harmonic model both C_{44} and $\nu(\text{E}_{2g})$ depend only on the relative lateral motion of undeformed basal planes. C_{44}-values estimated in this way have been found to be in reasonable agreement with experimental results for those metals which do not show high elastic anisotropy [4]. One attraction of equation (1) is that it gives estimates of the elastic constant C_{44} from E$_{2g}$ phonon frequencies under extreme conditions, e.g., very high pressures, where a direct experimental determination of the elastic constants is quite difficult or not possible at present. It is therefore of particular interest to examine whether this simple relation also holds for other types of solid. Here we examine its applicability to hexagonal van der Waals bonded phases of He, N$_2$ and solid hydrogens. None of these are simple solids: monatomic helium and the diatomic hydrogens are quantum crystals of large zero-point energy. Rotational quantum effects, but of different nature, are important for the H$_2$- and N$_2$-type crystals. At ambient pressure, H$_2$, D$_2$ as well as ^{4}He crystallize in hcp lattices below their melting points, and β-N$_2$, the hexagonal-close-packed phase of nitrogen, is stable between 35.6 and 63.1 K [5–7].

† The hcp lattice has two atoms or molecules per unit cell and thus six phonon branches in all, three acoustic and three optical. At the zone centre there is one LO mode, polarized along the c-axes, and two degenerate TO modes with polarization within the hexagonal planes. The latter one is the E$_{2g}$ mode in the spectroscopic notation. This phonon is a shear mode corresponding to the beating of the two hcp sublattices against each other in the two orthogonal directions in the basal plane.

For an elastically isotropic hexagonal crystal, the three anisotropy ratios

$$A_1 = 2C_{44}/(C_{11} - C_{12}) \qquad A_2 = C_{33}/C_{11} \qquad A_3 = C_{12}/C_{13} \qquad (2)$$

must be simultaneously equal to unity [8]. These three ratios are shown in figure 1 for ^{4}He [15], the hydrogens [9–12] and nitrogen [13, 14]. One can note that β-N_2 is close to being an elastically isotropic crystal, whereas the hydrogens exhibit elastic anisotropies at normal pressure, as expressed by the high A_3-values, which is perhaps not surprising in view of their large anharmonicity due to zero-point energy. It is evident that under compression more isotropic conditions are approached—similar to those found in the metals for which equation (1) gave reasonable estimates of C_{44} [4].
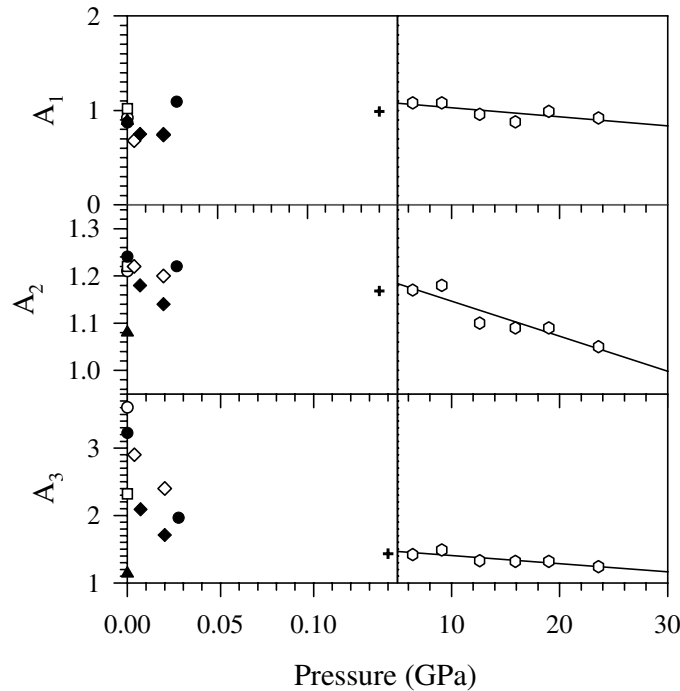

Figure 1. Anisotropy ratios for van der Waals bonded solids. Open circles: p-H_2 [9]; open squares: p-H_2 [11]; open diamonds: n-H_2 [10]; solid circles: o-D_2 [9]; solid diamonds: n-D_2 [10]; crosses: ^{4}He [15]; solid triangles: β-N_2 [14]; open hexagons: n-H_2 [12].

2. Results and discussion

For examination of equation (1) it is necessary to know C_{44}, $\nu(E_{2g})$, a and c for the same P–T conditions. For He, these data were obtained by neutron scattering studies [15]. The same holds for the hydrogens [9], where in addition Raman [16–19] and x-ray diffraction data [20–25] can be used. For β-N_2, Brillouin scattering [13, 14] provides data for C_{44} and lattice constants are available from x-ray diffraction data [26]. Though for normal pressure no frequencies of the TO mode were reported for β-N_2, a reasonable estimate of the ambient-pressure frequency is obtained by extrapolating the frequency–volume dependence of this mode [27] to the normal-pressure volume.

In table 1, C_{44}-values calculated from equation (1) are compared with experimental C_{44}-values. C_{44} calculated in this way agrees well, within 10%, with the experimental C_{44}. The uncertainties in the lattice parameters are typically 0.05% [9, 15, 20, 21, 26]; for the phonon frequencies they range from 0.13% for unusually precise Raman data on the hydrogens up to 15% in the case of β-N_2 [9, 15, 16, 27] which propagate also to the calculated C_{44}. Since the typical uncertainties in the frequency determination are usually 1 cm^{-1}, a more stringent test of equation (1) can be made at higher E_{2g} frequencies. For normal H_2, the E_{2g} phonon was shown to increase in frequency to the 1000 cm^{-1} range under pressures as high as 100 GPa [17–19]. Figure 2 shows C_{44}-values up to 100 GPa calculated from high-pressure E_{2g} frequencies [19] and lattice parameters [23–25] using equation (1). Below 10 GPa the experimental C_{44}-values [13], which have uncertainties in the region of 5%, are slightly lower (10%), but better agreement at higher pressures gives some confidence in the C_{44}-estimates in the 100 GPa regime. Also shown are C_{44}-values for D_2 calculated from the frequencies [19] and lattice parameters [22, 23]. At low compression, H_2 and D_2 have nearly identical values of C_{44}, but with increasing pressure the increase in C_{44} for H_2 is lower than for D_2. This effect, also manifested in the phonon frequencies [19], has been related to anharmonic perturbations in the intermolecular potential or, assuming a harmonic potential, to differences in the structural behaviour between H_2 and D_2 [19]. As regards the phase transitions occurring at higher pressures [28], it was suggested that the low-pressure phase might be stabilized to higher pressures in the heavier isotope (D_2) [19], which suggests in turn that the observed slight softening of the E_{2g} mode or C_{44} for H_2 relative to those of D_2 might be associated with this phase transition. Such a behaviour would parallel somewhat the observations made for hcp metals, where negative frequency shifts and weakening of C_{44} have been observed coincident with the occurrence of phase transitions [4, 29–31].

Table 1. Experimental and calculated C_{44} at or near normal pressure.

	a (Å)	c (Å)	ν (cm^{-1})	C_{44} (GPa), calculated	C_{44} (GPa), experimental
β-N_2, $T = 55$ K	4.088 ± 0.001[a]	6.687 ± 0.001[a]	20 ± 3[b]	0.38 ± 0.11	0.35 ± 0.007[c]
^{4}He, $P = 0.14$ GPa, $T = 8.3$ K	3.011 ± 0.002[d]	4.908 ± 0.002[d]	38.8 ± 2.7[d]	0.28 ± 0.039	0.24 ± 0.012[d]
^{4}He, $P = 0.37$ GPa, $T = 10$ K	2.807 ± 0.002[d]	4.58 ± 0.002[d]	50.2 ± 0.6[d]	0.50 ± 0.012	0.566 ± 0.012[d]
Para-H_2, $T = 5.4$ K	3.7837 ± 0.001[e]	6.1788 ± 0.001[e]	37 ± 1[f]	0.10 ± 0.05	0.11 ± 0.01[f]
Para-H_2, $T = 4.2$ K	3.7836 ± 0.001[e]	6.1785 ± 0.001[e]	36.79 ± 0.05[g]	0.105 ± 0.0003	
Ortho-D_2, $T = 5$ K	3.607 ± 0.001[f]	5.877 ± 0.001[f]	38.3 ± 1.2[f]	0.226 ± 0.06	0.23 ± 0.01[f]
Ortho-D_2, $T = 4.2$ K	3.603 ± 0.001[h]	5.885 ± 0.001[h]	35.83 ± 0.05[g]	0.20 ± 0.0006	

[a] Reference [26].
[b] Reference [27].
[c] References [13, 14] interpolated to 55 K.
[d] Reference [15].
[e] Reference [20].
[f] Reference [9].
[g] Reference [16].
[h] Reference [21].

Failure of equation (1) might be expected if the assumptions made in the derivation are not valid, i.e., if interactions beyond adjacent basal planes become important, or if anharmonic effects have to be considered. For the van der Waals solids considered here, departure from equation (1) is small, though some of them—the hydrogens and He near normal pressure—are distinguished by large anharmonicities due to their large zero-point energy. Equation (1) is also valid for hydrogen at high pressure, where one might possibly expect interactions between
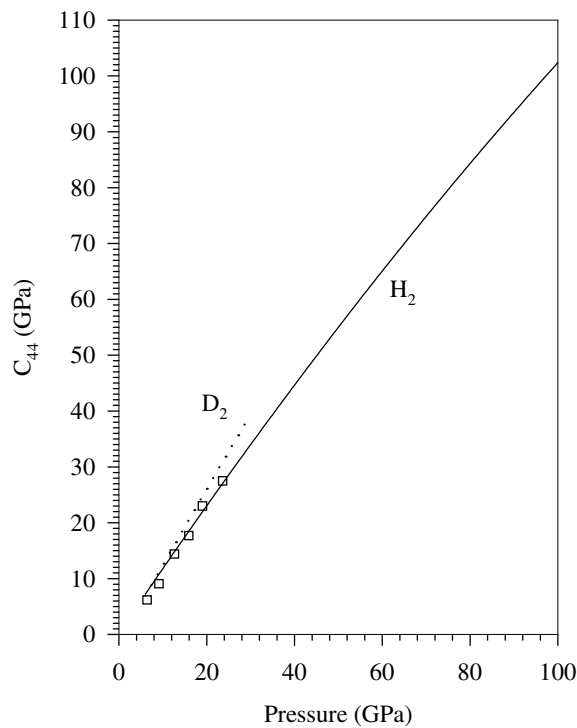
Figure 2. Calculated C_{44} (H_2, D_2) and experimental C_{44} (H_2) [12] as functions of pressure. The solid and dotted lines represent calculated C_{44} for n-H_2 and n-D_2, respectively. Open squares show Brillouin scattering data [12].

non-adjacent planes to become non-negligible. Note that a pressure of 24 GPa corresponds to approximately fivefold compression of solid H_2 [23, 25].

Although there is no obvious theoretical link with elastic isotropy, the metals for which equation (1) does not work well are Zn, Cd, Tl and to some extent Be, which all show large elastic anisotropies [4]. In Zn and Cd the distances to out-of-plane neighbours are different from those in the basal plane and their linear compressibilities differ considerably [32], which manifests itself in a high elastic anisotropy. This anisotropy is well known to be caused by the asymmetric charge distribution of the p electrons in these metals [33]. In the scheme used for derivation of equation (1) the electronic structure is not explicitly considered, so part of the interatomic interaction is not incorporated in the model; this might be why equation (1) does not work well for these metals. Similar arguments may also apply for Be, which is distinguished by an anisotropy, though not strong, in the p-electron-derived DOS [34]. For Tl we could not find data on the electronic structure, but the unusual shear anisotropy A_3 [4] might point to peculiarities in the bonding properties, which are determined to a great extent by the electronic structure in metals.

In a recent paper, Fast *et al* [35] showed that most of the hcp transition metals depart from the Cauchy relations $C_{13} = C_{44}$ and $C_{12} = C_{66}$ much less than their cubic counterparts, and concluded that their elasticity and lattice dynamics might be reasonably well described by means of central forces. The Cauchy relations strictly apply to static or harmonic crystals in which central forces alone operate, and even then only to those C_{ij} which are not associated with relative motions of sublattices; for the hcp structure, the only relation is $C_{13} = C_{44}$,

although a simple central-force model [3] indicates that departures from $C_{12} = C_{66}$ due to sublattice motion are likely to be fairly small. However, some of the Cauchy ratios for the van der Waals crystals shown in figure 3 differ from unity by factors up to three, indicating either strong anharmonic effects or that the forces are not central in nature. In particular, there is no correlation between the validity of equation (1) and observance of the Cauchy relations.
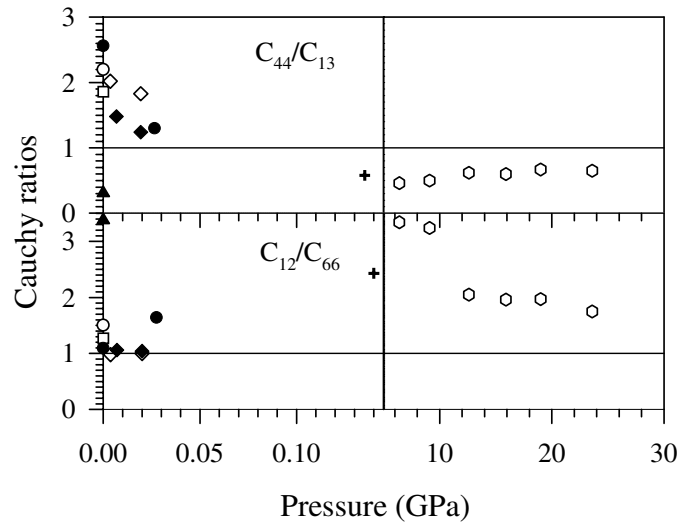

Figure 3. The Cauchy relation for van der Waals bonded solids. The assignments and the references are the same as for figure 1.

3. Summary

In summary, we have shown that a simple expression for C_{44} in terms of E_{2g} phonon frequencies and lattice parameters for hcp crystals, derived previously from a lattice dynamical, three-body force model, gives a reasonable estimate for the elastic constant C_{44} of the van der Waals bonded solids N_2, He and the hydrogens. Since this relation applies well also to most of the hcp metals, it is suggested that E_{2g} phonon frequencies can serve as a proxy for this particular elastic constant in hcp solids in general.

Acknowledgments

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