What is the nature of the A–phase of solid hydrogen?

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Phil. Trans. R. Soc. Lond. A 1998 **356**, 263-266
doi: 10.1098/rsta.1998.0162

What is the nature of the A-phase of solid hydrogen?

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Density functional calculations on the A-phase of compressed, solid hydrogen reveal the existence of a two-dimensional metallic state, involving the spontaneous polarization of constituent diatomic molecules.

Keywords: metallic hydrogen; density functional theory; high pressure phase; two-dimensional metal

1. Introduction

Ever since the prediction of Wigner & Huntingdon (1935) that hydrogen at sufficiently high pressures should be metallic, an unrelenting quest to squeeze hydrogen to ever higher pressures has yielded a fascinating and complex phase diagram. While several high-pressure phases have been discovered, none appears to be metallic. The so-called A-phase (or phase III) is stable at pressures in excess of approximately 150 GPa for both isotopes H_2 and D_2, and its properties and nature are somewhat of a mystery. It was originally discovered through the observation of a discontinuous softening of the Raman active vibron frequency (Hemley & Mao 1988; Lorenzana *et al.* 1989), and attributed to a structural and/or electronic transition. The possibility of it being an insulator–metal transition has been widely debated, but compelling evidence is lacking. Owing to great experimental difficulties to measure directly the conductivity at high pressures, the question of metallicity has been probed with optical experiments, fitting the reflectivity to a Drude model. In such a model, the reflectivity is expected to rise for incident radiation below the plasma frequency. Although early reflectivity experiments conducted down to frequencies of 4000 cm^{-1} appeared to show a rising reflectivity, recent experiments (Chen *et al.* 1996; Hemley *et al.* 1996) which probed to lower frequencies of 1000 cm^{-1} did not show a continuously rising reflectivity, thereby shedding considerable doubt on the metallic hypothesis. Such measurements, however, are not conclusive, since the phase may have anomalous optical properties. Most remarkable is the fact that the A-phase is IR active, a feature that is lacking in lower pressure hydrogen, and whose origin remains unexplained. Thus there are three questions of outstanding interest: (1) what is the structure of the A-phase?; (2) is it metallic, and if so, what is the nature of the metallicity and how can this be reconciled with the observed reflectivity?; (3) what is the origin of the IR activity of the A-phase?

In the absence of experimental data, the question of structure has been approached using density functional theory (DFT) (Kaxiras *et al.* 1991; Kaxiras & Broughton 1992; Nagara & Nakamura 1992; Edwards *et al.* 1996) and quantum Monte Carlo (Natoli *et al.* 1995). Until the work of Edwards & Ashcroft (1997), it was assumed

Phil. Trans. R. Soc. Lond. A (1998) **356**, 263–266
Printed in Great Britain

TEX Paper

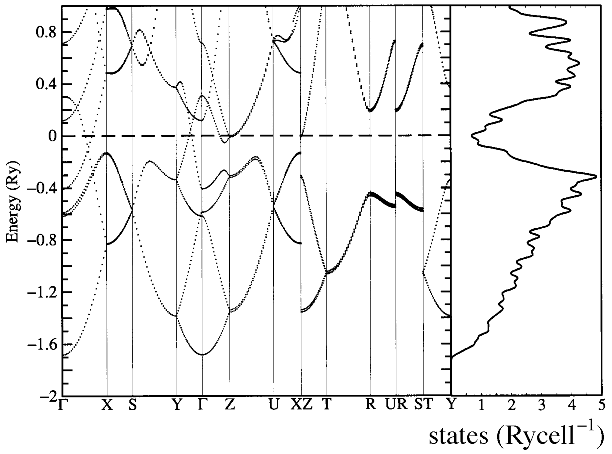

Figure 1. Band structure of the A-phase at $r_s = 1.43$. Note that the bands clearly cross the Fermi energy (0 Ry) in the $\Gamma \rightarrow X$ and $\Gamma \rightarrow Y$ directions, indicating two-dimensional metallic behaviour. The symbols refer to the high-symmetry points of the Brillouin zone of the primitive orthorhombic cell.

that the structure of the A-phase, in common with the lower pressure phases, is hexagonal-close packed (HCP), this supposition being based on the observation that a Raman active phonon at 1000 cm^{-1} is apparently not affected by the transition. Thus the theoretical calculations searched for low-energy structures assuming that the centres of mass to be fixed in HCP lattice sites. Edwards & Ashcroft (1997) were the first to show that, at pressures relevant to the A-phase, a family of orthorhombic structures becomes competitive in energy to the HCP one, and indeed at ninefold compression (pressures of approximately 150 GPa) an orthorhombic structure ($Cmca$) was lower in energy, both in static and dynamic approximations. Since then this general result has been confirmed (J. Kohanoff, personal communication; Alavi 1998).

Here we give a preliminary account of the results obtained by the present author, which will be published more completely elsewhere (Alavi 1998).

2. Computational details

We have performed DFT calculations within the local density approximation (LDA), supplemented with gradient corrections (GGA). We used the method of Alavi *et al.* (1994), with k-point meshes of 4^3 and 8^3. A pseudo-potential was employed for the proton–electron interaction, and the electronic orbitals were expanded up to 70 Ry. Following Edwards *et al.* (1996), we considered orthorhombic unit cells, consisting of eight atoms, with $b/a = \sqrt{3}$, so that both HCP and orthorhombic structures could be studied with the same cell. The c/a ratio was fixed at 1.6.

3. Results and discussion

Static minimizations, lattice dynamics and molecular dynamics calculations have been performed at a range of densities spanning the A-phase phase-boundary. We started at low density ($r_s/a_0 = 1.5$, $P \approx 120$ GPa; r_s is the electron sphere radius, $\rho = \frac{3}{4}\pi r_s^3$), with a $Pca2_1$ structure and relaxed it; the structure remained HCP. Next

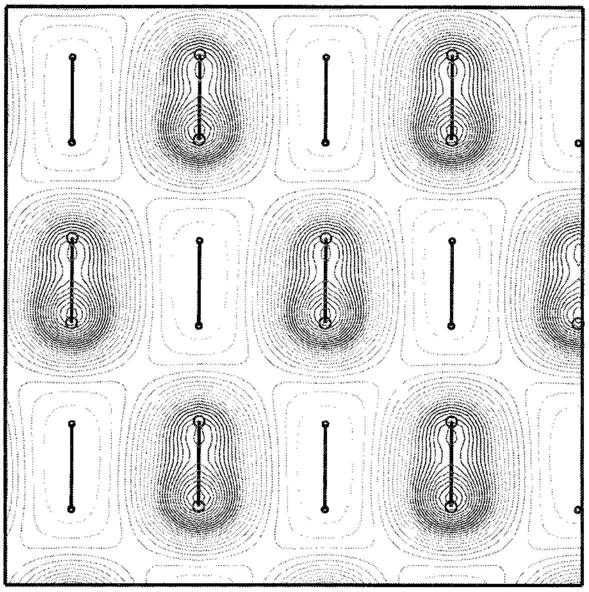

Figure 2. Charge density contours in the (a, b)-plane. The plane of the contours cuts symmetrically through the centre of the molecules. The polarization of the molecules is evident. The molecules in the layer below are polarized in the opposite direction (not shown).

a gradual compression was made, at each density fully relaxing the coordinates, upto a maximum density of $r_s = 1.42$. During this compression, the structure remained HCP. However, at the last state point, a large discontinuous increase in the bond length of the H_2 dimer was found. Strikingly, when the unrelaxed HCP configuration at $r_s = 1.42$ was perturbed slightly, giving each atom a small random displacement, the system was found to relax spontaneously to an orthorhombic structure. The relaxation of the molecules occurs in the (a, b)-plane, with molecules in alternate layers shifting parallel to the b-axis. The resulting relaxed structure, however, was a distorted $Cmc2_1$ structure, rather than $Cmca$, with protons displaced by small amounts from the perfect lattice sites. In a similar procedure to the compression, the $Cmc2_1$ structure was gradually decompressed. This structure remained stable until a density of $r_s = 1.48$, at which point it relaxed irreversibly back into an HCP structure. The bond lengths of the H_2 dimer are very different in the HCP and orthorhombic phases, being 5% longer in the latter phase. From a total energy viewpoint, the orthorhombic structure is more stable than the HCP at $r_s < 1.45$.

The band-structure of the orthorhombic phase is shown in figure 1. There is clearly a non-zero density of states at the Fermi energy, with the bands crossing in the $\Gamma \rightarrow X$ and $\Gamma \rightarrow Y$ directions. *The system is a two-dimensional metal, with conductivity allowed in the* (a, b)*-plane*. We have checked the effect of varying the k-point mesh and cut-off, and the GGA approximations, and in all cases we obtain similar results. The main features of band structure can be well reproduced using a simple tight binding model with sp bands. The metallicity is in part due to the lengthing of the H_2 dimer bond length in the orthorhombic phase. The intramolecular proton–proton distance is 0.77 Å, whereas the nearest intermolecular proton–proton distance is 1.22 Å, this distance being between two protons in the (a, b)-plane. This close proximity of the next-nearest proton enables the electrons to move from one proton to the next in the (a, b)-plane, thus forming a two-dimensional metal. The overlap of the bands is so great (of the order of 0.6 Ry) that the effect is very unlikely to be an artefact of the well-known band-gap problem of local density theory. If, as we are suggesting, the system is a metal, this leaves the question of its reflectivity to which we return below. We note that the reflectivity is expected to be highly anisotropic, mirroring the two-dimensional nature of the metal.

The charge density within the (a, b)-plane is shown in figure 2. The remarkable feature displayed here is the *polarization* of the H_2 dimers, a result also obtained very recently by Edwards & Ashcroft (1997) for an insulating system. The molecular dipoles in the (a, b)-plane are ferroelectrically aligned, whereas in alternative planes in the c-axis they are anti-ferroelectrically aligned. The appearence of the spontaneous polarization resolves the question of the IR activity of the A-phase, since the polarized molecules have IR active vibrons. The spontaneous polarization correlates with the fact that the proton lattice is distorted. This feature, as Edwards & Ashcroft note, is characteristic of a charge-density wave (CDW). CDW occur in the alkali metals (Overhauser 1971) and in layered quasi-two-dimensional systems, giving rise to anomalous optical absorption at low energies. We tentatively speculate that similar effects may be operative in the CDW observed here in the layered orthorhombic two-dimensional metal.

4. Conclusions

In conclusion, the picture of the A-phase sketched here is that the phase is a two-dimensional metal exhibiting a charge-density wave in the form of a spontaneous polarization of the molecules. There is converging theoretical agreement that the phase is probably orthorhombic. The spontaneous polarization, similar to that obtained by Edwards & Ashcroft (1997) for insulating orthorhombic structures, explains the IR activity of the A-phase. In contrast, however, we predict two-dimensional metallic behaviour. We are currently investigating the optical properties of our model, which we expect to exhibit anomalies similar to those found for other metals with charge-density waves.

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