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ENERGY GAP OF MOLECULAR HYDROGEN FROM ELECTRICAL CONDUCTIVITY MEASUREMENTS

W. J. NELLIS, A. C. MITCHELL, D. J. ERSKINE, P. C. MCCANDLESS, and S. T. WEIR

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

Electrical conductivities were measured for liquid D_2 and H_2 shock-compressed to pressures of 10-20 GPa (100-200 kbar), molar volumes of 9.0-7.2 cm^3/mol, and calculated temperatures of 2900-4600 K. The semiconducting energy gap derived from the conductivities is in good agreement with recent quasiparticle calculations and with oscillator frequencies measured in diamond-anvil cells.

1. INTRODUCTION

The density dependence of the electronic energy bandgap of hydrogen is of great current interest with respect to the insulator-metal transition. Since the valence-conduction bandgap of solid hydrogen is about 15 ev at zero pressure, very high pressures are required to close the gap and achieve metallization. Measurements of the frequency dispersion of the refractive index $n(\omega)$ of solid hydrogen in a diamond cell yield effective oscillator frequencies ω_1, which correlate closely with the energies of direct valence-conduction band transitions.[1-3] Quasiparticle calculations of the electronic bandgap of H_2 place bandgap closure and the insulator-metal transition at 150 and 300 GPa, respectively, for c-axis aligned and orientationally disordered H_2 in the hcp phase at 0 K.[4] Intermolecular potentials derived from Raman vibron data,[5] indicate that the fully dissociated metallic transition occurs at about 300 GPa.[6]

The purpose of this paper is to report measurements of electrical conductivities of hydrogen at high pressures. Because shock compression is used, the associated high temperatures activate electron carriers and enable determination of the semiconducting energy gap E_g. Also, the high shock temperatures cause nearly constant-volume states in D_2. Thus, shock pressure is varied primarily to vary temperature and carrier concentration. A major issue to be resolved is the substantial difference between H_2 energy gaps calculated theoretically by LDA[7-9] versus quasiparticle methods[4] using various crystal structures. At the volumes of our experiments the LDA and quasiparticle[10] energy gaps are about 7 and 12 ev, respectively.

2. EXPERIMENT

Theoretical analysis[11] of EOS data of single-shocked liquid H_2 and D_2[12-14] showed that the molecular fluid phase is stable to above 20 GPa shock pressure and that shock temperatures range up to 4600 K (0.4 ev) at 20 GPa for D_2. Since the molar volume of D_2 decreases threefold at 20 GPa shock pressure, E_g should decrease from its initial value of about 15 ev[15] to the 12 ev range.[10] E_g can be derived from measured electrical conductivities using the equation for a liquid semiconductor:

$$\sigma = \sigma_o \exp(-E_g / 2k_BT). \quad (1)$$

Since the shock temperatures T are small compared to the gap energy, the highest possible shock temperatures are required to induce measurable conductivities. Most experiments were performed, therefore, with liquid D_2 specimens, because the maximum available shock pressures and temperatures are appreciably higher for D_2 than for H_2.[11,14]

Shock compression was achieved by accelerating planar Ta impactors with a two-stage light-gas gun[16] to measured velocities in the range 5.2-6.7 km/s and impacting them onto Al specimen holders.[17] The cryogenic holders[14] were cooled with liquid H_2. Electrical conductivities were measured using a two-probe method, similar to that used for liquid O_2 and N_2 experiments.[18,19]

3. RESULTS

Three conductivity points were measured for shocked D_2 in the range 13-20 GPa and 7.8-7.2 cm^3/mol. Calculated shock temperatures are in the range 2900-4600 K.[11] The data were plotted as $\log(\sigma)$ vs T^{-1} and fit Eq. 1. The vari-

ation in molar volume is small. Thus, these compressions are quasi-isochoric and the variation in E_g with volume can be neglected. An experiment was performed with liquid H_2 at 10.0 GPa, 9.0 cm^3/mol, and 3000 K. The measured conductivity agrees with the exponential pressure dependence of the conductivity predicted from the quasiparticle bandgaps at H_2 shock volume,[10] the calculated shock temperatures of H_2,[11] and σ_0 obtained from the D_2 data.

Our energy gap of D_2 is 12 ev at 8 cm^3/mol, in good agreement with the quasiparticle calculations.[10] Our value of E_g also agrees well with measured optical oscillator frequencies of about 12 ev at 7 cm^3 of solid H_2.[1-3]

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