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High pressure phase transition in metallic LaB_6: Raman and X-ray diffraction studies

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Abstract

High pressure Raman and angle dispersive X-ray diffraction (ADXRD) measurements on the metallic hexaboride LaB_6 have been carried out upto the pressures of about 20 GPa. The subtle phase transition around 10 GPa indicated in Raman measurements is confirmed by ADXRD experiments to be a structural change from cubic to orthorhombic phase. Ab-initio electronic band structure calculations using full potential linear augmented plane wave method carried out as a function of pressure show that this transition is driven by the interception of Fermi level by electronic band minimum around the transition pressure.

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1. Introduction

Hexaborides (MB_6) can be monovalent metals or semiconductors [1] depending on whether the metal ion M is trivalent or divalent, respectively, because the B_6 molecule in them needs two electrons from the metal to stabilize the divalent B_6 state. LaB_6, a monovalent and non-magnetic metal, is of great technological importance as thermionic cathodes in electronic devices with high performance characteristics [2]. In the intermediate valence compounds CeB_6 and SmB_6, the elastic constant C_{12} is negative while in LaB_6 it has a very small positive value [3–5]. The breakdown of Cauchy relation (small value of C_{12} compared to the larger C_{44}) in LaB_6 is an indication of presence of volume-dependent long range forces. Such long range forces are speculated to be arising due to the occupied part of the conduction band formed by the anti-bonding orbitals of the B_6 molecules and the 5d e_g-orbitals of La atoms [6]. The fact that volume dependence can lead to violation of Cauchy relation and the small value of C_{12}, is evident from the behavior of C_{12} and C_{44} of mixed valence $Sm_{1-x}Y_xS$ with variable metal size and the divalent YbB_6 [5]. Application of pressure will result in an energy shift of the anti-bonding B_6 orbitals leading to a rise in the conduction band causing further lowering of C_{12} to induce structural changes under pressure. However, the pressure variation of electrical resistance and thermoelectric power of LaB_6 up to 10 GPa show a monotonic decrease [7] while that of divalent YbB_6 and EuB_6 suggest [8] evidence of mixed valence state at pressures above 10 GPa. The present work aims to investigate the high pressure behavior of LaB_6 experimentally using Raman and X-ray diffraction measurements. Also the first principles electronic band structure

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