

Kelly, Dekker, and Stumpf Reply: On the basis of neutron powder diffraction (NPD) measurements on YD_3 [1,2] the symmetry of YH_3 is believed to be $P\bar{3}c1$. Local density approximation (LDA) calculations of the electronic structure were carried out for this so-called HoD_3 structure by Dekker *et al.* [3] and by Wang and Chou [4]. They found two partially occupied bands at the Fermi level which overlap by more than 1 eV so that YH_3 should be metallic. Very recently, simultaneous electrical and optical measurements on novel thin film samples were made as a function of the hydrogen concentration and strong evidence presented that YH_3 is in fact a large band gap semiconductor [5]. This would seem to imply a discrepancy between experiment and the Kohn-Sham eigenvalue spectrum (calculated within the LDA) comparable only to what is found in highly correlated materials such as the $3d$ transition metal oxides [6].

Yttrium undergoes a volume expansion of about 17% when it absorbs three hydrogen atoms per yttrium atom. Because of the possibility that strain might stabilize thin film YH_3 in a structure different to that found in the bulk, we carried out total energy calculations within the LDA and minimized the energy with respect to the atomic positions as a function of strain. In Ref. [7] we reported finding a broken symmetry structure with a large band gap whose energy was slightly lower than that of the HoD_3 structure even for the equilibrium (bulk) lattice constants. We suggested that the NPD measurements might have missed this structure because of the general difficulty of detecting the absence of certain symmetry elements in racemic mixtures. A number of weak additional diffraction lines are predicted for the new structure whose intensity is comparable to the background noise in the room temperature data published by Udovic *et al.* [2]. In the preceding Comment Udovic *et al.* report on an extended search for and failure to detect the predicted lines [8]. The measurements were carried out at low temperature so that thermal broadening can be excluded as an explanation.

Before dismissing symmetry lowering as an explanation for the metal-insulator transition, a number of possibilities should be considered. First, the positions of the H atoms in thin-film YH_3 have not been determined experimentally; the structure in the thin films may be different to that of the bulk material studied with neutrons. Second, the role of the wave nature of the hydrogen or deuterium atoms should be examined. In particular, it may be necessary to consider the zero point motion of the metal plane and near-metal-plane hydrogen atoms in the shallow potential confining them in the empty channels along the c axis. Udovic *et al.* have measured the phonon density of states (DOS) using inelastic neutron scattering and have identified a low frequency 57 meV peak in the DOS with this motion [9].

Assuming for simplicity that this frequency corresponds to the motion of a single H atom in a harmonic potential then the corresponding root-mean-square displacement of a D atom in the z direction is 0.16 Å which is comparable in size to the “anomalously” large rms displacement of 0.29 Å observed in the NPD [2]. Detailed calculations are needed to determine whether the zero point motion makes a significant temperature independent contribution to the Debye-Waller factor. A third possibility is posed by the observation that the rms displacement estimated above is comparable to the symmetry-breaking hydrogen displacements. It is possible that the hydrogens are in a superposition of broken symmetry states making their experimental observation very difficult. In this case the electrical properties at low temperature would be determined by the volumes of configuration space sampled by the zero point motion which are “metallic” and “semiconducting.”

Even if the high symmetry metallic configuration should turn out to have a lower energy than the broken symmetry semiconducting configuration in a more accurate (than LDA) static calculation, we would expect the symmetry to be dynamically broken by the zero point motion of the H atoms. In this case a large isotope effect might be expected.

P.J. Kelly,¹ J.P. Dekker,² and R. Stumpf³

¹Philips Research Laboratories

Prof. Holstlaan 4

5656 AA Eindhoven, The Netherlands

²Faculty of Physics and Astronomy, Vrije Universiteit

De Boelelaan 1081

1081 HV Amsterdam, The Netherlands

³Sandia National Laboratories

Albuquerque, New Mexico 87185-1413

Received 25 July 1997

[S0031-9007(97)04259-2]

PACS numbers: 71.30.+h, 71.15.Pd, 61.12.-q

- [1] N.F. Miron *et al.*, Sov. Phys. Crystallogr. **17**, 342 (1972).
- [2] T.J. Udovic, Q. Huang, and J.J. Rush, J. Phys. Chem. Solids **57**, 423 (1996).
- [3] J.P. Dekker, J. van Ek, A. Lodder, and J.N. Huiberts, J. Phys. Condens. Matter **5**, 4805 (1993).
- [4] Y. Wang and M.Y. Chou, Phys. Rev. Lett. **71**, 1226 (1993); Phys. Rev. B **51**, 7500 (1995).
- [5] J.N. Huiberts *et al.*, Nature (London) **380**, 231 (1996).
- [6] K.K. Ng *et al.*, Phys. Rev. Lett. **78**, 1311 (1997); R. Eder, H.F. Pen, and G.A. Sawatzky (to be published).
- [7] P.J. Kelly, J.P. Dekker, and R. Stumpf, Phys. Rev. Lett. **78**, 1315 (1997).
- [8] T.J. Udovic, Q. Huang, and J.J. Rush, preceding Comment, Phys. Rev. Lett. **79**, 2920 (1997).
- [9] T.J. Udovic, J.J. Rush, Q. Huang, and I.S. Anderson, J. Alloys Compd. **253–254**, 241 (1997).