

Comment on "Theoretical Prediction of the Structure of Insulating YH_3 "

In their recent Letter, Kelly *et al.* [1] reported the use of density functional calculations of the total energy to determine the minimum energy structures for hexagonal YH_3 . They concluded that, although YH_3 is found to be metallic in the high-symmetry ($P\bar{3}c1$) HoD_3 structure [2] in agreement with the work of Wang and Chou [3], there exists a lower-energy, broken-symmetry ($P3$) structure possessing a large band gap. Such a band gap is consistent with the interpretations of optical and electrical measurements on YH_x by Huiberts *et al.* [4]. However, this broken-symmetry structure is inconsistent with our recent neutron powder diffraction (NPD) data for YD_3 [5], which were successfully refined using the high-symmetry structure.

Kelly *et al.* [1] suggested that the symmetry breaking due to the small hydrogen displacements may not be possible to observe in an NPD experiment since an intermixing of "left-handed" and "right-handed" configurations of the $P3$ structure occurs. We have reexamined our NPD data in light of this suggestion. For our $P\bar{3}c1$ structure, c -glide symmetry restricts the allowable Bragg reflections to $(h0l)$ where $l = 2n$ for integer values of n . For the proposed $P3$ structure, assuming that the "different-handed" crystallites are large on a neutron length scale, the lack of c -glide symmetry would remove these restrictions, leading to additional reflections. This is exemplified in Fig. 1, which compares a portion of the fit to our data for the $P3$ structure. The fit takes into account the large thermal ellipsoids associated with the deuterium atoms aligned along the axes of threefold symmetry, although the sharpness of the corresponding deuterium optic-vibrational modes measured by neutron spectroscopy is indicative of well-defined lattice positions. Figure 1 indicates that the $(10\bar{3})$ and (103) reflections, while forbidden for $P\bar{3}c1$ symmetry, are allowed for $P3$ symmetry and should provide a combined observable intensity above the background. Yet there is a clear absence from our data of these reflections as well as all other additional reflections expected, which leads to a relatively poorer goodness of fit for the $P3$ structure. Moreover, refinements of models possessing $P\bar{3}c1$ symmetry (i.e., excluding only inversion symmetry) fail to converge due to high correlations between the positions of the near-centrosymmetric atoms.

These results verify beyond doubt that $P\bar{3}c1$ symmetry is preserved for YD_3 . Hence, it appears that the only possible way to reconcile the inconsistencies between the $P3$ structure and our NPD data is to assume that an average $P\bar{3}c1$ symmetry exists via an appropriate microtwinning of the $P3$ structure, with the untwinned microdomains only of the order of a few unit cells in size. Yet model fits using such a structure are less than satisfactory. Among the shortcomings are a poor agreement with the expected site occupancies of the deuterium atoms and a tendency of

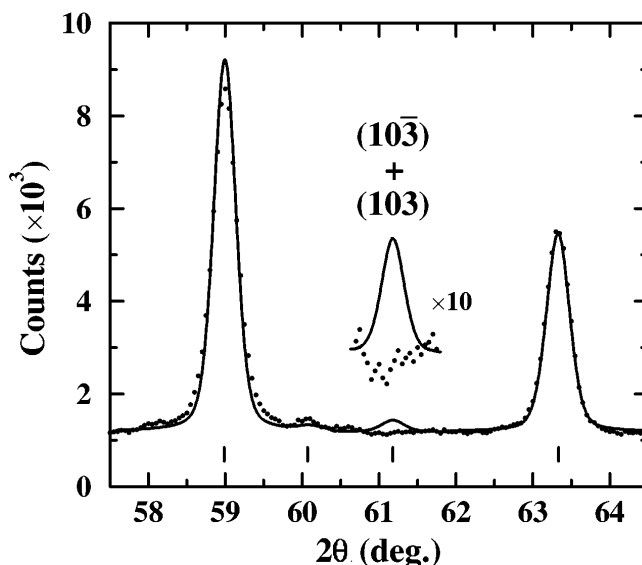


FIG. 1. A portion of the fit of the $P3$ structure (solid line) to the 16 K NPD data for YD_3 . The vertically expanded region is offset by -9×10^3 counts. The bars beneath the data mark the calculated positions of the allowable reflections. The data were collected using the NIST high-resolution BT-1 diffractometer with a $\text{Ge}(311)$ monochromator and a wavelength of $2.0775(1)$ Å.

the fit to place the near-metal-plane deuterium atoms much closer to the metal plane than predicted by theory.

In conclusion, it would seem that further work is needed to establish a structure that is fully consistent with both the diffraction data and the novel physical properties associated with YH_3 and related rare-earth trihydrides.

T. J. Udovic, Q. Huang,* and J. J. Rush
NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001

Received 17 April 1997 [S0031-9007(97)04258-0]
PACS numbers: 71.15.Pd, 61.66.-f, 71.30.+h, 71.55.Ak

*Also at the Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD 20742.

- [1] P. J. Kelly, J. P. Dekker, and R. Stumpf, *Phys. Rev. Lett.* **78**, 1315 (1997).
- [2] M. Mansmann and W. E. Wallace, *J. Phys. (Paris)* **25**, 454 (1964).
- [3] Y. Wang and M. Y. Chou, *Phys. Rev. Lett.* **71**, 1226 (1993); *Phys. Rev. B* **51**, 7500 (1995).
- [4] J. N. Huiberts, R. Griessen, H. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, *Nature (London)* **380**, 231 (1996).
- [5] T. J. Udovic, Q. Huang, and J. J. Rush, *J. Phys. Chem. Solids* **57**, 423 (1996).