Direct Observation of $(B_{12})(B_{12})_{12}$ Supericosahedra as the Basic Structural Element in YB_{66}

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Solids containing boron icosahedra have structural elements common to many materials of current interest. For example, a B_{60} shell with the same structure as C_{60} is part of the structure of elemental boron. The boron-rich solids can thus provide insights into the structural properties of a variety of seemingly unrelated materials. Here scanning tunneling microscopy images of $YB_{66}(100)$ are reported that reveal B_{156} supericosahedra as discrete structural entities. While the structure of YB_{66} is formally described in terms of such supericosahedra, this is the first evidence of their existence as stable units in their own right. [S0031-9007(96)01763-2]

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Materials containing units of icosahedral symmetry have recently received much attention in a variety of different contexts. Icosahedral arrangements of thirteen atoms are common in gas phase metal clusters [1]. However, objects of icosahedral symmetry cannot fill three-dimensional space and most solids utilize a lower symmetry unit cell to achieve the efficient packing densities possible with periodic structures. Some quasicrystals do have icosahedral symmetry and therefore necessarily have aperiodic structures [2]. The prototypical fullerene C_{60} has icosahedral symmetry and therefore an understanding of how icosahedral units can be linked to form a solid is highly relevant to understanding the structural properties of fullerene materials [3]. In contrast to these more recent topics, descriptions of the structures of many of the boron-rich solids have long invoked icosahedral arrangements of boron atoms [4]. The β-rhombohedral boron structure is conveniently described in terms of a B_{84} unit that consists of a central B_{12} icosahedron with each vertex linked by a single boron atom to the pentagonal faces of an outer B_{60} shell. This B_{60} shell has exactly the same buckyball structure as C_{60} [4]. Another example is provided by the MB_{66} structure, where M is one of several metals including yttrium, which is usually described in terms of so-called supericosahedra consisting of 13 B_{12} icosahedra. These B_{156} [or more descriptively, $B_{12}(B_{12})_{12}$] units are composed of a central B_{12} icosahedron with 12 B_{12} icosahedra bonded to each of the 12 vertices of the central B_{12} unit. However, it has not been at all clear if these boron supericosahedra have structural stability as discrete entities within the overall crystal structure, or are merely convenient conceptual constructs used for describing the structure. The latter viewpoint is suggested by the fact that many of the B-B bonds between supericosahedra are shorter than the bonds within the supericosahedra. This would imply that the boron atoms are merely part of an undifferentiated extended three-dimensional network. However, we report here scanning tunneling microscope (STM) images of the (100) surface of a single crystal of YB_{66} that clearly reveal that large boron clusters are stable as discrete units within the material.

Although this is both the first STM study, as well as the first surface science study of any MB_{66} material, the bulk crystal structure of YB_{66} has been thoroughly characterized [5–10]. The structure is based on a face centered cubic (fcc) lattice (lattice constant $= 23.44$ Å) with a unit cell that contains approximately 1600 boron atoms, of which 1248 are assigned to eight B_{156} units. The remaining boron atoms have been assigned to disordered nonicosahedral structures consisting of B_{48} units or a mixture of B_{48} and B_{36} units. More recent work assigns the nonicosahedral boron to a B_{80} unit in which only 50% of the sites are occupied [10]. The yttrium atoms randomly occupy approximately 50% of the metal atom sites, giving about 25 yttrium atoms per unit cell. Figure 1 is a schematic representation [8] of the $YB_{66}(100)$ surface. Two types of B_{156} units, which differ only by a 90° rotation, are shown. There are four channels of fourfold symmetry between the B_{156} units in each (100) face. Both the nonicosahedral boron and the yttrium atoms are located in these channels. It is important to stress that although the material is only 1.6 at. % yttrium, it is a stoichiometric compound with a structure that is quite different from pure boron. It is a common theme in the boron-rich solids that electron deficient, covalently bonded networks of boron atoms can exist only if they are stabilized by the donation of electrons from a metal. This explains, in part, why in the structure of β-rhombohedral boron, the most stable form of the pure element, a smaller fraction of the boron atoms have the preferred icosahedral bonding environment than in YB_{66}. This illustrates a general feature among the boron-rich solids that utilize B_{12} icosahedral in their structures: The greater the fraction of the boron atoms that have

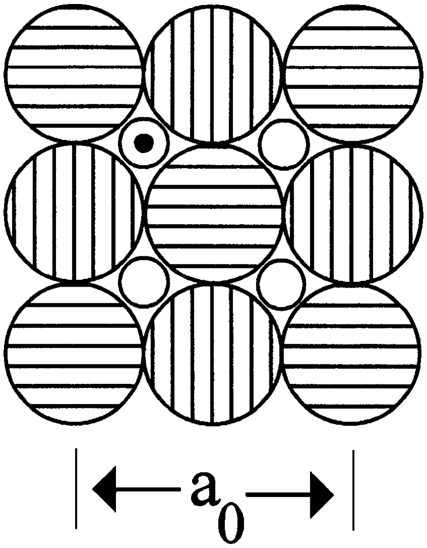

FIG. 1. A schematic (after Ref. [8]) of the YB_{66}(100) surface. Each of the larger circles represents a nearly spherical "supericosahedron" of 156 boron atoms in a $B_{12}(B_{12})_{12}$ arrangement, with adjacent supericosahedra differing by a 90° relative rotation. Smaller circles represent nonicosahedral boron units, and the small black dot one of the yttrium atoms randomly distributed in the channels between B_{156} supericosahedra.

the preferred icosahedral bonding environment, the more complex is the structure, with YB_{66} being the most extreme example yet found. Thus a more detailed understanding of the structure of YB_{66} can provide a better understanding of the trade-offs involved in the more general problem of utilizing structural units of icosahedral symmetry in solid materials.

The two single crystal samples used here were grown by a crucible-free floating zone method that has been described in detail elsewhere [11–13]. The growth conditions were optimized to obtain crystals of high enough quality to use as x-ray monochrometers. They were cut from single-crystal boules by spark erosion, oriented to within 0.5° of the (100) direction and polished to a mirror finish. The room temperature resistivity of YB_{66}, which is a semiconductor, is reported to be several hundred Ω cm [8,13]. The STM measurements were made in an ultrahigh vacuum (UHV) chamber (base pressure $<5 \times 10^{-11}$ torr) that has been described in detail elsewhere [14]. In short, the UHV chamber is equipped with low energy electron diffraction (LEED) optics, a quadrupole mass spectrometer, an STM, a system for x-ray photoelectron spectroscopy (XPS), a sputter ion gun for sample cleaning, and facilities for sample heating and cooling. The crystal was cleaned within the UHV chamber by a combination of heating to 1500 K and Ar ion bombardment. Extremely sharp LEED patterns indicative of a square lattice with lattice constant of 23.4 Å were routinely obtained. The ratio of yttrium to boron in the surface region, as determined from XPS measurements following heating to 1500 K, was the same as in the bulk. The LEED and XPS measurements, which will be described in detail elsewhere [15], indicate that the material evaporates congruently without surface reconstruction and is thus amenable to study by standard surface science techniques. This basic fact had not been established prior to our work. Imaging with the STM was performed in a constant current mode at room temperature and was typically initiated two hours after sample cleaning in order to minimize thermal drift. Tips for the STM were prepared by electrochemically etching tungsten wire and were cleaned *in situ* by electron bombardment and field desorption. The STM piezotube expansion coefficients were determined from atomically resolved images of a Si(111) (7×7) surface encompassing regions having one or more steps. All STM images shown here have been plane filtered.

Figure 2(a) is a topograph over a 1000×1000 Å^2 area that shows broad (100) oriented terraces separated by

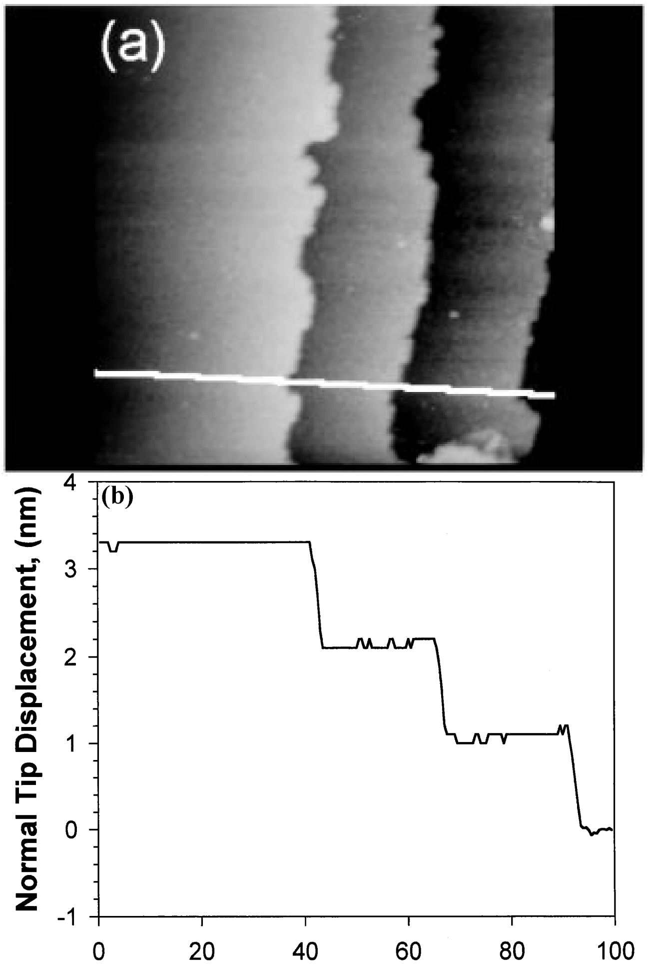

FIG. 2. (a) A large scale (1000 Å)^2 STM image showing several half unit cell high steps separating (100) terraces. The image was taken with the sample at -5 V relative to the tip and a tunneling current 1 nA. A single line scan across these steps is shown in (b).

steps. The size of the terraces seen on the two $YB_{66}(100)$ surfaces examined varied, with about half having widths greater than 1000 Å. The basic appearance of the image of Fig. 2(a) is typical of that of other single crystal samples, which inevitably show terrraces of the nominal crystal orientation with steps at an average density related to how accurately the sample was cut. In metals and many semiconductors the steps are one atom in height, a consequence of the fact that individual atoms are the fundamental structural units in most solids. However, a feature that was constant in all of our STM images of the $YB_{66}(100)$ surface was the step height of 11.7 ± 0.7 Å, which, within the accuracy of the measurement, is half the unit cell length of 23.44 Å. The fact that the step height is equal to the distance along the (100) direction between adjacent B_{156} units is one indication that these supericosahedra constitute stable structural entities within the solid. Another indication of this is manifested by the roughness of the step edges, which have irregularities on the scale of one to a few B_{156} units.

The image in Fig. 3 shows a 500×500 Å area revealing a periodic array of objects along with numerous defects and vacancies. The numerous images of this surface that have been obtained over the course of this study, including the one shown in Fig. 4, show that the grid is a two-dimensional square lattice with a lattice constant of 11.7 Å. The distortions from a perfect square lattice that are evident in Fig. 3 are due to thermal drift over the course of the five min required to obtained the image. Although an STM image strictly only reveals the two-dimensional distribution of electron density near the Fermi level, for lack of any information to the contrary we assume that there is a close correspondence between the distribution of atoms and electrons at the surface. Referring to Fig. 1, it is seen that if the relative orientation of the two-inequivalent B_{156} units is ignored, then these units form a square lattice of 11.72 Å on a side. The nonicosahedral boron units and the yttrium atom sites would also form an 11.7 Å square lattice. However, the fact that the yttrium sites are partially and randomly occupied implies that imaging of the metal atoms would yield a more disordered structure than observed. Also, angle-dependent XPS measurements indicate that the topmost surface layer consists of boron rather than yttrium [15]. Since the electron density at the lattice points is too delocalized to be associated with single boron atoms, the images must be indicative of an 11.7 Å square array of boron clusters. These clusters may be the bulklike clusters or an arrangement that is specific to the surface. The fact that the bulklike nonicosahedral clusters are described as being disordered [6–10] would seem to be incompatible with the highly regular array seen in Figs. 3 and 4. Distinguishing between bulklike B_{156} clusters and a surface specific cluster might be possible if structure could be resolved within the units. Attempts to do so have so far been unsuccessful, perhaps due to the delocalized nature of the bonding within boron clusters. Nevertheless, the images of Figs. 3 and 4 are entirely consistent with an array of B_{156} supericosahedra arranged with the same periodicity as in a bulk (100) plane. Hence in the following discussion the boron clusters that are imaged in Figs. 3 and 4 will be referred to as B_{156} units with the caveat that confirmation of this particular point will require additional work. Figure 4 also shows that the vacancies correspond to the absence of whole B_{156} units whereas other defects correspond to displacement of these units from their ideal lattice positions. Plots of vertical tip displacement as a function of horizontal displacement in ⟨100⟩ directions indicate a corrugation of over 1 Å. While such a high corrugation

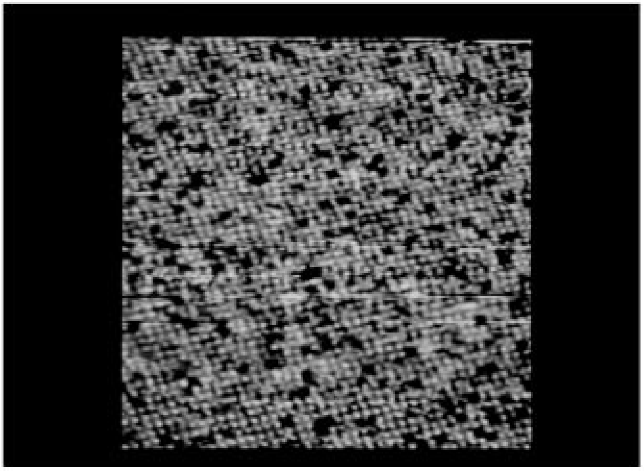

FIG. 3. A $(500\ \text{Å})^2$ image of a large (100) terrace in which a defect marred lattice is clearly visible. This image, taken at 5 V and 1 nA, is slightly skewed by thermal drift occurring during the rather slow (5 min) scan.

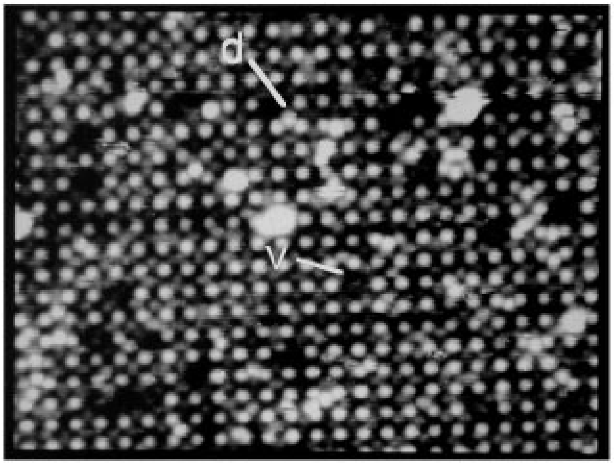

FIG. 4. A small scale ($288\ \text{Å} \times 216\ \text{Å}$) image of a (100) terrace in which the square lattice of supericosahedra is apparent. Defects appear as displacements (d) or vacancies (v) of complete 11.7 Å diameter components, another indication of B_{156} supericosahedron stability. Features between the B_{156} units display considerably more disorder. The image was taken at a -3.5 V bias and a tunneling current of 0.5 nA.

between B_{156} units makes it easy to resolve them, it also makes a superimposed atomic corrugation that is expected to be on the order of 0.1 Å more difficult to detect.

In addition to the pronounced structure associated with the B_{156} units, structure between the units is apparent in Fig. 4. However, there is a great deal of variation in the appearance of this structure from one unit cell to the next. As indicated in Fig. 1, both the nonicosahedral boron cages as well as the Y atom sites would lie along the fourfold channels. However, as noted earlier, the Y atom sites are partially and randomly occupied. Furthermore, previous work has revealed much greater disorder associated with the nonicosahedral boron than with the B_{156} units. In a thorough x-ray diffraction study of the YB_{66} structure, Richards and Kasper [7] concluded that the fourfold channels were occupied with equal probability by either B_{48} or B_{36} units. This conclusion was based on disorder associated with the nonicosahedral boron atom positions. A similar degree of disorder for the nonicosahedral boron was recently found for YB_{66} crystals grown under the same conditions as the crystals used here [10]. There is thus ample reason to suspect that the lack of periodic order for the structure observed within the fourfold channels is intrinsic to the YB_{66} crystal and not specific to STM observations of the surface structure.

Given the inherently complex structure of YB_{66}, the most striking feature of the STM images is their simplicity. Although the simplicity in itself is quite informative, many important questions remain unanswered. For example, assuming the topmost layer consists of whole B_{156} units, then surface formation involves the breaking of bonds between B_{156} supericosahedra and breaking bonds within the nonicosahedral boron structures leaving several types of so-called dangling bonds at the surface. In many instances, pairing of such coordinatively unsaturated bonds leads to surface reconstructions. In this case, reconstructions within the B_{156} units that did not alter the periodicity would not be observed. Having established that YB_{66} is amenable to study by surface science techniques means that future studies can focus on the more detailed features of the surface structure. Nevertheless, the work reported here has already established one fact of central importance: Large boron clusters, presumed to be B_{156} supericosahedra, exist as stable discrete entities within the YB_{66} crystal. This conclusion is based on the uniform step height of 11.7 Å, by irregularities at step edges on the scale of the B_{156} units, by the presence of whole B_{156} unit vacancies and defects, as well as by the well-resolved 11.7 Å square lattice of B_{156} units. While the B_{156} unit has long been used in formal descriptions of the YB_{66} structure, there was little prior basis for anticipating the results presented here. Slack *et al.* [8] showed a transmission electron microscope image of YB_{66} in the (100) direction in which a square grid of objects, which they identified as B_{156} units, was observed. Richards and Kasper [7] found that the radial bonds connecting the outer icosahedra to the central icosahedron of a B_{156} unit were substantially shorter than bonds within the icosahedra. This might have suggested that these radial bonds would not be broken in forming the surface. However, the bonds linking B_{156} units are shorter than some of the bonds within the units. Thus bond lengths alone would not imply any particular stability of the B_{156} units as discrete entities. The existence of such discrete units as the fundamental building block in a crystal with three-dimensional periodicity has important implications for the structure of other solids possessing units of icosahedral symmetry.

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