

Electronic Structure and X-Ray Raman Spectrum of Solid Boron

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An extensive experimental and theoretical study of the x-ray Raman spectrum and electronic structure of polycrystalline boron has been performed. Anomalous peaks in the spectrum are directly related to the structure of the electronic density of states at high unoccupied bands. The present technique can probe the density of states very deep in the unoccupied conduction bands. The *d*-like nature of the "anomalous" peaks leads to a dipole approximation reevaluation.

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The electronic structure of crystalline boron is not known accurately because of its complicated crystal structure with many atoms per unit cell. Solid boron appears in at least two different crystal forms, tetragonal and rhombohedral, both based on the icosahedron geometry. The simplest form, which is rhombohedral with twelve atoms per unit cell, is shown in Fig. 1 in a projection on the (001) plane of the related hexagonal unit cell.¹ The icosahedron geometry is also common in many important boron compounds. Groups of twelve atoms, in elemental boron and in many boron-rich compounds, are tightly bonded together in icosahedra that behave as large pseudoatoms with a diameter of ≈ 5 Å. These pseudoatoms can stick together in various packings and accept guest atoms in the spaces in between. Since the basic unit of these complicated structures is the icosahedron, it is reasonable to model the system with a small cluster consisting of twelve boron atoms in the corners of only one of the four icosahedra shown.

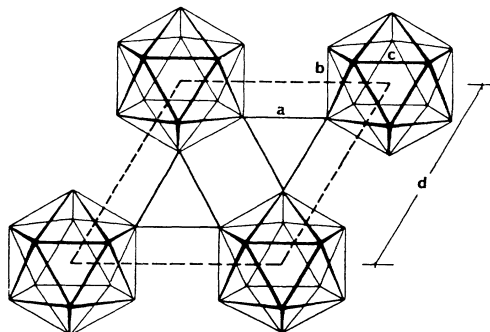


FIG. 1 The structure of rhombohedral boron projected onto the (001) plane of the related hexagonal unit cell. The distances a, b, c, d are $a=2.03$ Å, $b=1.78$ Å, $c=1.73$ Å, and $d=4.91$ Å (Ref. 1). The small cluster describing polycrystalline boron consists of the twelve atoms in the corners of only one of the four icosahedra shown.

been shown recently^{2,3} to provide a reasonably good and unified picture for simple elemental metallic and nonmetallic solids. The small-cluster description can provide not only bonding information but also phonon and structural properties^{2,3} and inner-core electron binding energies,^{4,5} as well as band-structure properties,^{6,7} such as Fermi energies and density of states (DOS). These states and DOS can extend very high in the conduction band where they can operate as virtual resonance states in appropriate scattering experiments.

Probing of these virtual states deep in the conduction band has become increasingly interesting recently, both experimentally and theoretically. It was implicitly illustrated earlier⁶ that a good experimental tool for the study of these states is energy-loss spectroscopy via the x-ray Raman scattering technique⁸⁻¹⁰ supplemented with the theoretical tool of *ab initio* small-cluster calculations. Specifically, it was shown for Be that a good understanding of the origin and nature of the observed "anomalous" peaks in the region of the x-ray Raman band was achieved by a small-cluster description of Be metal.⁶

The present investigation for B aims in a similar way as the earlier investigation for Be at achieving both an understanding of the electronic structure and a good description of the anomalous x-ray Raman peaks. The search for anomalous peaks, which as in Be are nothing more than complex manifestations of the electronic structure above and around the Fermi level, is one of the primary reasons for undertaking the present investigation. A few representative articles on the x-ray Raman scattering and related work are cited by Suzuki and Nagasawa,¹¹ Eisenberger and co-workers,¹² Wendin,¹³ and Alexandropoulos.¹⁴

The experimental setup for the energy-loss x-ray spectroscopy, underlying the x-ray Raman measurements, has been described before.¹⁵ It consists mainly of a Rigaku-Denki (type RU-200PL) 12-kW rotating-anode

x-ray generator, with a Cu target and a flat single-crystal spectrometer. The x-ray tube was operated at 55 kV and 180 mA and the spectrometer resolution was $E/\Delta E \approx 1100$. The scatterer was powder of polycrystalline boron. To achieve a good accuracy the spectra were obtained by step scanning, using a fixed-time counting method and the Cu $K\beta$ line. The spectra were scanned five times for every scattering angle and the statistical error was 1.3%. The step of the scanner was 0.01 and the time duration of each step was 400 s.

The theoretical framework for the calculations is based on the small Hartree-Fock cluster technique.²⁻⁷ According to this technique, which has been shown to be quite successful, a small number of atoms is used to simulate the infinite crystalline system. The actual number of atoms in the cluster depends upon the property under study. It is quite clear from the discussion on the crystalline forms of boron that a twelve-atom cluster with icosahedral geometry describes well the structural unit of boron in all of its forms. The twelve atoms are placed in the corners of one of the four icosahedra shown in Fig. 1.

The Gaussian basis functions for B have been contracted out of the Huzinaga set¹⁶ and have been enhanced with virtual d orbitals. The cluster Hamiltonian is formed and diagonalized by the unrestricted Hartree-Fock (UHF) method.¹⁷ In the UHF, contrary to the usual restricted Hartree-Fock method, the spin-up and spin-down pairs are not restricted to have the same spatial wave function and the orbitals are not required explicitly to have the symmetry properties of the point group of the crystal. The standard POLYATOM computer code was used to compute the integrals and the program UHFABK of Kunz was employed to perform the UHF calculations.

Carrying out the program outlined in the previous section, we have plotted in Fig. 2(a) the energy-loss spectrum displaying clearly the Raman bank around 200 eV and the anomalous peaks in the region of 280 eV quite far from the x-ray Raman band. This spectrum is taken at a scattering angle of 55° , but the position of the anomalous peak remains the same for all scattering angles. In the same Fig. 2(a), the results of the calculation in the region of the Fermi level and the region of 300 eV above the $1s$ level are superimposed in the form of an energy-level diagram. In Fig. 2(b) the simulated DOS at this energy region is displayed. This simulated DOS, as explained before,^{6,7} is constructed from the energy-level diagram by a suitable Gaussian broadening. It becomes immediately clear that both the Raman band and the anomalous peak structure around 280 eV are well reproduced in the calculated energy-level diagram and DOS of Fig. 2. The states around the Fermi level (i.e., the highest occupied orbital) producing the Raman band are of atomic p type with a small admixture of s -type orbitals. The states responsible for the anomalous peak

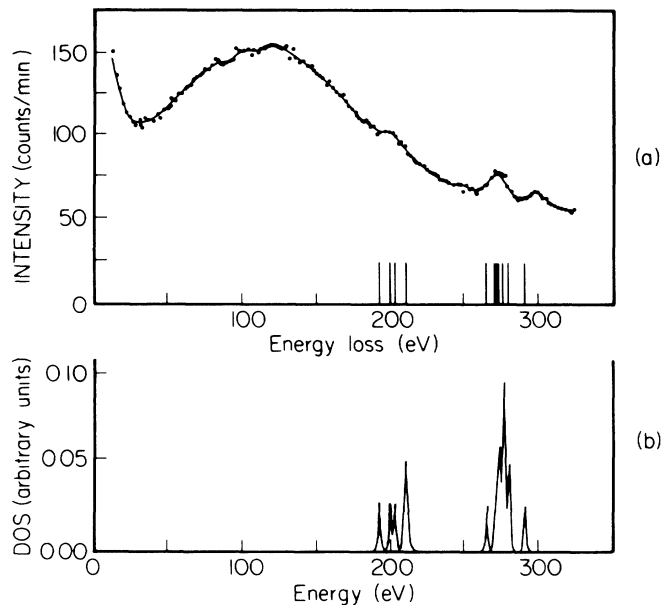


FIG. 2 (a) The measured x-ray Raman spectrum and the calculated energy level diagram together with (b) the simulated DOS in the energy region shown. The points in the spectrum represent the actual measurements. The line through the points is the result of a spline fit.

structure in Fig. 2 are of d character with a small admixture of s - and p -type states. The energy splitting between d orbitals of different symmetries and of different percentages of s and p admixture results in a rather large width for the corresponding anomalous peak. Relative to the Raman peak, the height of the anomalous peak seems to be larger because, perhaps, of the more compact nature of the d orbitals, compared to the sp orbitals responsible for the Raman peak.

The valence band of boron is dominated by the p orbitals with a rather small s admixture. In Figs. 3(a) and (b), the bonding characteristics of the states at the bottom and top ("Fermi level") of the valence band, respectively, are displayed in the form of constant-amplitude contours. The three-center bonds, which are believed to be responsible for the lack of metallic behavior in B, are rather clearly visible in Fig. 3(a). The picture at the Fermi level is slightly more complicated.

We have been able to investigate and identify both theoretically and experimentally the x-ray Raman peak and the anomalous peak structure at 280 eV of polycrystalline boron. Such a peak structure has been observed and theoretically identified for the first time. Our results demonstrate the ability of the x-ray Raman scattering technique to probe the DOS very high in the conduction bands (almost 100 eV from the highest occupied state, i.e., the Fermi energy).

The *ab initio* description of the electronic structure of polycrystalline boron, based on icosahedron clusters of

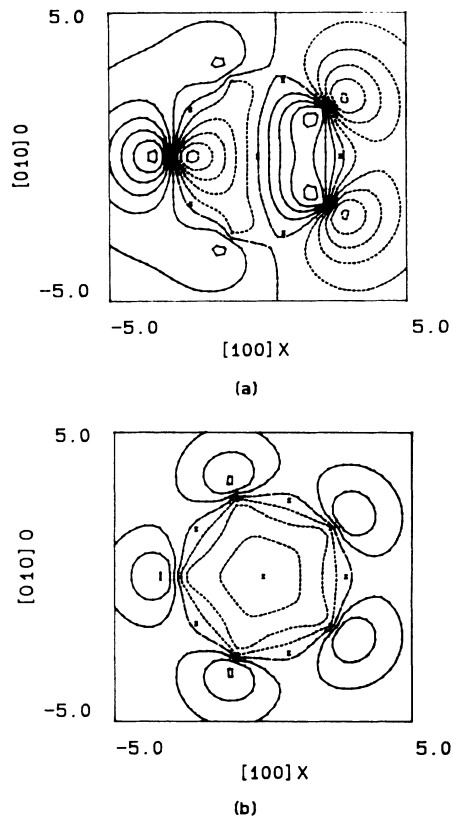


FIG. 3 The orbitals at (a) the bottom and (b) the top of the valence band in constant-amplitude contours. The contours are shown on a horizontal plane through five boron atoms. The projections of the boron atoms on this plane are shown with crosses. Solid curves represent positive amplitudes, dotted curves represent negative amplitudes, and dashed curves denote zero amplitudes. The contour step is 0.01.

twelve boron atoms, seems to be both adequate and unique, in the sense that it reproduces well the major electronic features of B on a very large energy scale and it is the first time that such a calculation has become available. Our cluster description of the electronic structure provides an unambiguous association of the anomalous peak, observed in our measurements, with d -like atomic states. This in turn presents a novel case of an apparent dipole selection-rule violation. Certainly for a solid and this deep in the continuum energy region, it is difficult to access the validity of dipole selection rules based on the atomistic angular momentum notion.

However, on the basis even of a loose application of dipole selection rules, one would expect that such "nonallowed transitions" would be somewhat inhibited. On the contrary, as can be seen in Fig. 2, our present results show an enhancement of such transitions. At this time, it is not clear to us whether or not the compactness of the d orbitals especially in this three-center bonding configuration could offer a plausible explanation for the observed enhanced anomalous peak structure.

Nonetheless, the angular dependence of the spectrum that we have set to examine in a forthcoming publication¹⁸ does justify the departure from dipole behavior.

¹See, for instance, P. J. Brown and J. B. Forsyth, *The Crystal Structure of Solids* (Crane, Russak, New York, 1973).

²A. D. Zdetsis, *Phys. Rev. B* **34**, 7666 (1986).

³A. D. Zdetsis, *Phys. Rev. B* **35**, 5868 (1987).

⁴C. A. Nicolaides, A. D. Zdetsis, and A. N. Andriotis, *Solid State Commun.* **50**, 857 (1984).

⁵A. D. Zdetsis, in *Proceedings of the International Conference on X-Ray and Inner-Shell Processes, X87, Paris, September 1987* (to be published).

⁶A. D. Zdetsis and D. Miliotis, *Solid State Commun.* **42**, 227 (1982); A. D. Zdetsis, unpublished.

⁷A. D. Zdetsis and A. B. Kunz, *Phys. Rev. B* **32**, 6358 (1985).

⁸Y. Muzuno and Y. Ohmura, *J. Phys. Soc. Jpn.* **22**, 445 (1967); M. Kuriyama, *Acta Crystallogr., Sect. A* **27**, 634 (1971).

⁹T. Suzuki, *J. Phys. Soc. Jpn.* **22**, 1139 (1967); T. Suzuki, T. Kishimoto, T. Kaji, and T. Suzuki, *J. Phys. Soc. Jpn.* **29**, 730 (1970); R. Johnston and D. Tomboulian, *Phys. Rev.* **94**, 1585 (1954).

¹⁰T. Sagawa *et al.*, *J. Phys. Soc. Jpn.* **21**, 2602 (1966).

¹¹T. Suzuki and H. Nagasawa, *J. Phys. Soc. Jpn.* **39**, 1579 (1975).

¹²P. Eisenberger and P. M. Platzman, *Phys. Rev. B* **13**, 934 (1976); P. Eisenberger, P. M. Platzman, and P. Schmidt, *Phys. Rev. Lett.* **34**, 18 (1975).

¹³G. Wendin, *Phys. Scr.* **21**, 535 (1980).

¹⁴N. G. Alexandropoulos, *J. Phys. Soc. Jpn.* **31**, 1790 (1971).

¹⁵D. K. Papadimitriou and D. M. Miliotis, *J. Phys. Soc. Jpn.* **51**, 2966 (1982).

¹⁶S. Huzinaga, "Approximate Wave Functions I" (unpublished).

¹⁷A. B. Kunz, in *Theory of Chemisorption*, edited by J. R. Smith, *Topics in Current Physics*, Vol. 19 (Springer-Verlag, Berlin, Heidelberg, 1980).

¹⁸D. K. Papadimitriou and A. D. Zdetsis, to be published.