Lattice Dynamics of Icosahedral α-Boron under Pressure

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The Raman spectrum of icosahedral α-boron presents a very sharp peak at 525 cm^{-1} that was consistently rejected from the lattice modes but is still unexplained. New Raman scattering experiments under pressure are compared with *ab initio* lattice dynamics calculations. The very good agreement of the mode frequencies and their pressure coefficients yields unambiguous assignment of all observed features, including the 525 cm^{-1} line which is a highly harmonic librational mode of the icosahedron and mainly involves bond bending. This mode is also identified in the Raman spectrum of other icosahedral boron-rich solids. [S0031-9007(96)02238-7]

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Elemental boron and boron-rich solids have various applications, and among them β-B_{105} boron [1] and boron carbides [2] are widely used in nuclear engineering. Their atomic structure is based on an arrangement of distorted B_{12} or $B_{11}C$ icosahedra. In these, the *intraicosahedral* three-center bonds present some analogy with metallic bonding because electron deficiency forces electrons to be shared at the surface of the icosahedron. Icosahedral structures are linked together by strong covalent bonds, so that the *intraicosahedral* and *intericosahedral* bonds have comparable strength [3]. Indeed, it has been recently found that in boron carbide, B_4C, intericosahedral bonds are surprisingly stiffer than intraicosahedral ones [4]. These properties make these materials interesting also from a fundamental point of view, in that they display features which are typical of both metals and semiconductors. This fact, together with the propensity of boron-rich solids for being assembled in icosahedral units, has recently prompted the attention onto these systems as candidates for semiconducting quasicrystals [5].

The simplest member of the family, α-boron, has a rhombohedral unit cell encompassing a slightly distorted B_{12} icosahedron. In Fig. 1 we display the structure of α-boron, which contains two inequivalent crystallographic sites. In the first, *polar*, site, six atoms form the upper and lower triangles that are related by inversion symmetry. The second site is *equatorial* and six atoms form a hexagon in the plane perpendicular to the [111] rhombohedral axis. The polar atoms form strong covalent intericosahedral bonds that are radially directed outwards. The equatorial atoms are involved in the Δ three-center bonds which form equilateral triangles in the plane perpendicular to the [111] axis. Among elemental semiconductors, α-boron is perhaps the least understood as regards its vibrational properties. In spite of the existence of a number of experimental [6] and theoretical [7] studies, the interpretation of the existing infrared and Raman spectra is still highly controversial: while only half of the expected infrared modes have been identified, its Raman spectrum shows more features than the ten lines expected theoretically. Particularly conspicuous is the case of the line observed by Raman spectroscopy at 525 cm^{-1}, whose vibrational nature has been so far denied on the basis of its exceedingly small linewidth and pressure coefficient.

So far, experimental investigations of phonons in α-boron have been restricted to optical techniques [8] since large enough α-^{11}B single crystals are not available for inelastic neutron scattering experiments. Previous theoretical work was based on force-field models fitted to infrared and Raman experimental data [7]. The resulting zone-center vibrational modes of α-B_{12} could be classified as follows: (i) *intericosahedral* modes with wave numbers

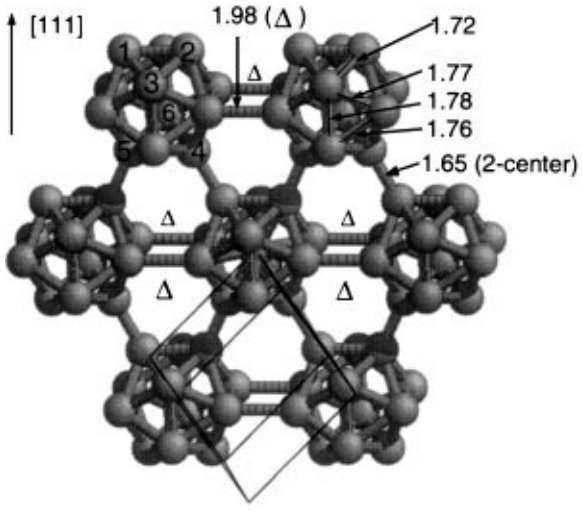

FIG. 1. Crystalline structure of α-B_{12}. Atoms 1–3 (4–6) form the upper (lower) polar triangle (1st site). Atoms 6–12 are quasiequatorial and form a distorted hexagon (2nd site). Bond lengths (Å) are at theoretical equilibrium.

above 1000 cm^{-1}; (ii) *intraicosahedral* modes between 950 and 550 cm^{-1}, that is, lower in frequency, which illustrates the fact that α-boron is an inverted-molecular structure [3]; (iii) *librational* modes, which involve rotations of the whole heavy icosahedron, and therefore would lie in the range 100–200 cm^{-1}. This classification does not account for the *ghost* line at 525 cm^{-1} whose full width at half maximum is indeed unusually small (FWHM < 1 cm^{-1}) [6]. Although different explanations for this unusual behavior and for the inability of lattice-dynamical models to account for any Raman-active mode near 525 cm^{-1} have been put forward—such as electronic Raman scattering or impurity processes [7]—the very nature of the ghost line is still unknown, and therefore a careful experimental and theoretical reinvestigation of the lattice dynamics of α-boron is called for. To this end, we have performed accurate Raman scattering measurements as a function of pressure up to 30 GPa, and *ab initio* calculations of the vibrational spectrum.

Our Raman spectra have been collected at room temperature from single α-B_{12} microcrystals grown from a palladium solution and—at ambient pressure—they are identical to previously published data [6]. Unpolarized light from the 5145 Å line of an argon laser was used for the excitation and the Raman light was analyzed with a DILOR *XY* triple spectrometer. Plasma lines from the argon laser have been eliminated by using a PELLIN-BROCA prism which has a rejection factor of more than 10^6 at 150 cm^{-1}. High pressure data were collected in a membrane diamond-anvil cell loaded with neon as a pressure transmitting medium. The pressure was evaluated with the nonlinear ruby luminescence scale.

Calculations were performed within density functional theory and density functional perturbation theory [9], using the local density approximation and the plane-wave pseudopotential method. The norm-conserving pseudopotential and the exchange-correlation energy functional are the same as in Ref. [10]. Plane waves up to a kinetic-energy cutoff of 55 Ry have been included in the basis set, and the irreducible wedge of Brillouin zone has been sampled with 10 points. Structural properties have been determined upon accurate geometry optimizations done at different volumes. In Table I, we report our results for the structural properties at equilibrium. At variance with the result reported in Ref. [4] for B_4C, we find that the icosahedral units are stiffer than intericosahedral space. The pressure derivative of the phonon frequencies has been determined from calculations made at two volumes, corresponding to a compression at $+12$ GPa and an expansion at -10 GPa.

In Fig. 2 we display the Raman spectrum of α-boron at ambient pressure, together with the pressure dependence of the observed peaks. α-boron has D_{3d} point symmetry [7] and the Raman-active modes correspond to 6 E_g doublets and 4 A_{1g} singlets at the center of the Brillouin zone. Our measured and calculated Raman-active frequencies, ω are reported in Table II along with their pressure coefficients, γ. No reproducible features were found below 500 cm^{-1}. The lowest frequency (*ghost* line) at 525 cm^{-1} shows an immeasurably small FWHM, within the resolution of our spectrometer (3 cm^{-1}). Compared to all the other lines, it shows a very weak variation

TABLE I. Calculated and experimental structural parameters of α-B_{12}. a is the lattice parameter; α is the angle between the rhombohedral lattice vectors (in degrees); $\langle r_{ico} \rangle$ is the mean radius of the icosahedron; d_1 (d_2) is the two-center covalent bond (Δ three-center bond). Lengths are in Å.

	a	α	$\langle r_{ico} \rangle$	d_1	d_2
This work	4.98	58.2	1.68	1.65	1.98
Expt.[a]	5.06	58.2	1.69	...	...
Expt.[b]	5.07	58.0	1.70	1.67	2.00

[a]From Ref. [17]
[b]At 0.5 GPa. From Ref. [18]

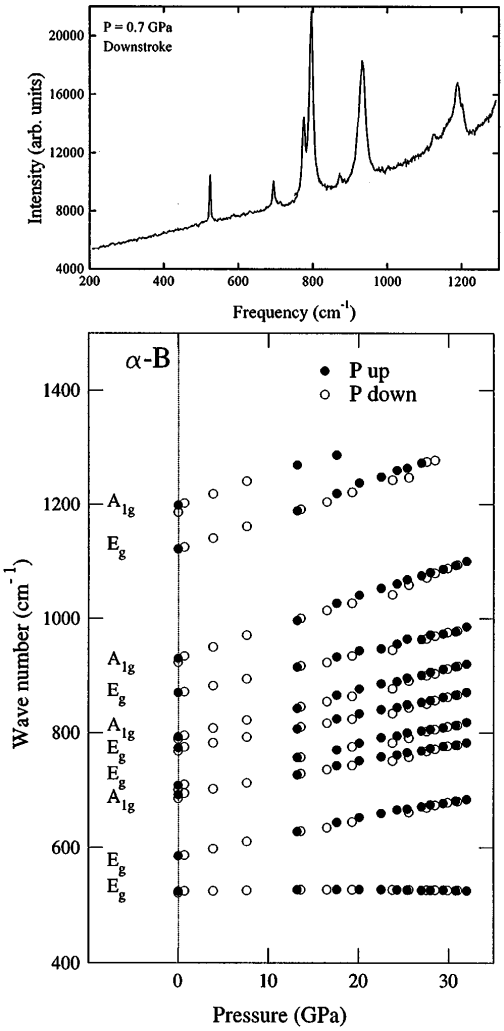

FIG. 2. Upper panel: Raman spectrum of α-boron at ambient pressure. Lower panel: experimental pressure dependence of the Raman lines: full (empty) dots: data collected when loading (unloading) the diamond-anvil cell.

TABLE II. Theoretical and experimental Raman frequencies at ambient pressure, ω (cm^{-1}), and their pressure coefficient, $\gamma_P = (\partial\omega/\partial P)_{P=0}$ ($cm^{-1}\,GPa^{-1}$). When it is measurable, the experimental FWHM at ambient pressure is given (cm^{-1}). The FWHM of the libration is taken from Ref. [13].

	E_g	E_g	A_{1g}	E_g	E_g	A_{1g}	E_g	A_{1g}	E_g	A_{1g}
ω_{th}	529	608	708	729	790	815	890	947	1138	1192
ω_{expt}	525	586	692	708	774	793	870	925	1122	1186
FWHM	0.8		5		7	11	8	22	15	24
γ_P^{th}	0.18	3.3	2.8	3.5	2.3	4.2	3.3	5.2	5.5	5.6
γ_P^{expt}	0.3	3.3	3.0	3.6	2.6	4.2	3.5	5.4	5.2	5.0

up to 30 GPa. By contrast, the high frequency mode at 1186 cm^{-1} has a complex structure with small shoulders at 1195 and 1160 cm^{-1} and a FWHM $\approx$22 cm^{-1}. We assign it to a single A_{1g} mode and attribute its width mainly to isotopic effects, as explained below.

A Raman-active vibrational mode of symmetry E_g is predicted at 529 cm^{-1}, very close to the experimental frequency of the *ghost* line ($\omega_{\text{exp}} = 525$ cm^{-1}). The agreement between theory and experiments is extremely good, the average error on individual modes being less than 2.5% with a maximum error that only in one case reaches 4%, for the E_g mode observed at 585 cm^{-1}. A similar accuracy is obtained for the infrared modes, which will be reported elsewhere [11], thus giving us confidence in the predictive power of our calculations for the mode assignments. Particularly important in this respect is the agreement within the actual precision of the measurements (0.6 cm^{-1} GPa^{-1}) between our calculated pressure coefficients and those experimentally observed.

The E_g mode at 529 cm^{-1} corresponds to a degenerate rotation of the whole icosahedron around one of the two axes orthogonal to the [111] rhombohedral axis. This assignment is at variance with the previous assumption that the librational mode would be well separated from the other kinds of vibrations, and indicates that bond bending is about as energetic as bond stretching. The other libration mode, about the [111] axis, is an A_{2g} silent mode found at 508 cm^{-1}. The two librational frequencies are very close, indicating that the crystalline environment is approximately isotropic for an angular displacement of the icosahedron, and that each type of intericosahedral bond yields the same contribution to the restoring force. Both experimental and theoretical results confirm that the pressure coefficient of the ghost line is more than an order of magnitude smaller than that of all other modes. It is worth mentioning that also the silent librational mode is predicted to have an unusually small pressure coefficient, $\gamma_{A_{2g}} \approx 0.1$ cm^{-1} GPa^{-1} [11].

The ghost line has been consistently observed as a strong peak in all of the spectra published so far [6], but its vibrational nature has always been rejected on the following grounds: (i) its FWHM is much smaller than that of the other vibrational lines and below the expected isotopic broadening; (ii) it has been detected for an oriented crystal for two independent directions of polarization of the incoming light, contrary to what selection rules would allow [12]; (iii) in some experiments, a would-be librational mode was found in the low frequency part the spectrum, at 175 [13] and 215 cm^{-1} [14]; they have not been reported in subsequent work and are therefore too uncertain to be included in a mode assignment scheme for α-boron. Finally, (iv) current lattice-dynamical models do not predict any Raman-active lines near 525 cm^{-1}.

The most precise determination of the experimental FWHM of the ghost line has been done by Tallant *et al.* [13], resulting in a value smaller than 1 cm^{-1} which is the usual resolution limit of most Raman setups. Assuming that the ghost line does correspond to a vibrational mode, a FWHM this small implies a long phonon lifetime, and therefore an inefficient process for its decay into two or more lattice vibrations. This would be the case either if a small density of vibrational states exists for the final states, or if the anharmonic interaction process is weak. Although the former hypothesis cannot be ruled out without a careful analysis of the phase space available to the products of the decay [15], we are rather inclined to believe that it is the anharmonic matrix element responsible for the decay which is indeed small. This is at least compatible with the small pressure coefficient of the mode—as observed experimentally and predicted theoretically—which is also mainly due to cubic anharmonicity, as is the phonon decay. A thorough analysis of the effects of anharmonic broadening and isotopic disorder on the width of the ghost line is beyond the scope of the present Letter and will be presented elsewhere. Here we limit ourselves to notice that—assuming that this line is due to a *rigid* rotation of the icosahedral unit—the corresponding frequency would vary as the inverse square root of its *total* mass whose maximum fluctuation due to the relative abundance of ^{10}B and ^{11}B is very small ($\approx$1.5%). Finally, we note that lattice modes as sharp as the ghost line have been reported in low-dimensional structures such as the intralayer shear modes of layered GaSe and GaS. They are consistently associated with very small pressure coefficient ($\gamma_P^{\text{exp}} <$ 1 cm^{-1} GPa^{-1}) and one-mode behavior in mixed GaS GaSe crystals [16].

Selection rules dictate that E_g modes are visible in the $Y(ZX)Y$ geometry, but not in the $Y(ZZ)Y$, while the reverse holds for A_{1g} modes. The detection of a signal at 525 cm^{-1} in the $Y(ZZ)Y$ geometry is one of the arguments that has led to conclude that this line cannot correspond to a E_g vibrational mode [12]. However the intensity of the signal is hardly 1% of that observed for the four *bona fide* A_{1g} structures. In the $Y(ZX)Y$ geometry, instead, the intensity of the ghost line is comparable to that of the most intense E_g mode observed at 775 cm^{-1}. We attribute the

observation of the ghost line in the "wrong" geometry to a small violation of the selection rules coming from the existence of various kinds of disorder and/or imperfect polarization of the laser light.

Finally, inspection of the Raman spectra of other boron-rich compounds strongly suggests that the similar Raman active lines in the boron pnictides $B_{12}P_2$ and $B_{12}As_2$ at, respectively, 518 and 508 cm^{-1} [13], and in boron carbide $B_{12}C_3$ at 535 cm^{-1}, have a librational character. As noted above, stretching plays a minor role in the libration, while intericosahedral bonds of any type, either two-center bonds or Δ bonds, are likely to have the same resistance to bending. Then, no major variation in the librational frequency is expected when the intericosahedral Δ bonds are replaced by conventional two-center bonds, as it is the case in boron pnictides and carbides. Isotopic enhancement experiments on the latter carbide [12] support this assumption: the observed frequency shifts of the modes at 535 cm^{-1} are 23.5 cm^{-1} between $^{10}B_{11}C$ and $^{11}B_{11}C$, and 1 cm^{-1} between $B_{11}{}^{12}C$ and $B_{11}{}^{13}C$. The libration frequency is proportional to the inverse square root of the mass of the $B_{11}C$ icosahedron so that the expected frequency shifts would be 23.6 and 2 cm^{-1}, which are precisely the observed shifts within the experimental error (± 1 cm^{-1}).

The four A_{1g} modes are breathing motions in which each one of the symmetry independent crystallographic sites has a different amplitude. The two A_{1g} modes at 692 and 1186 cm^{-1} (theory: 708 and 1192 cm^{-1}) are noticeable in that only one site vibrates in turn, while the other is quasi-immobile. The restoring force for these modes is mainly due to bond stretching: the mode at 692 cm^{-1} only stretches the weaker three-center Δ bonds, while in the other mode only the strong intericosahedral two-center bonds are stretched. Isotopic disorder might explain why the observed lines display such a large FWHM (22 and 24 cm^{-1} at 692 and 1186 cm^{-1}, respectively). As only six atoms vibrate in each one of these modes, the three statistically most probable mass distributions are $^{10}B_2{}^{11}B_4$, $^{10}B^{11}B_5$, and $^{11}B_6$. For the mode at 1186 cm^{-1} and in the narrow-band limit, this would lead to a frequency shift of ± 8 cm^{-1} which satisfactorily reproduces the line shape, although the intensity of the experimental shoulder found at 1160 cm^{-1} may also include two-phonon combinations from the low-frequency E_g modes. Whether or not the assumption of narrow phonon bands is justified and whether isotopic disorder and anharmonic broadening may account for the rather different linewidths observed for different modes is a matter that requires further investigations.

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