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Interband Transitions and Optical Phonons of $B_{48}Al_3C_2$

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The optical absorption edge of $B_{48}Al_3C_2$ has been measured. It is decomposed into several interband transitions between 0.97 and 2.5 eV. Additionally, several gap-state-related transitions with energies between 0.45 and 0.96 eV were determined. They are attributed to defects in the structure, whose character is not yet known. The spectra of IR- and Raman-active phonons and their resonance frequencies are presented. According to other icosahedral boron-rich solids, the phonons can roughly be separated into vibrations of icosahedra and those of single atoms. The vibrations of the tetrahedrally bonded Al1 atom are discussed in analogy to the tetrahedral XY_4 molecule. © 2000 Academic Press

Key Words: **tetragonal boron; interband transitions; electronic gap states; phonons.**

INTRODUCTION

The crystal structure of $B_{48}Al_3C_2$ has been controversially discussed (for a recent review and detailed discussion of the different structure models (see (1,2)). According to (1) the orthorhombic crystal structure (Fig. 1) with four formula units per unit cell is closely related to α-tetragonal boron (tetragonal boron I), and consists of bars formed by icosahedra interconnected along one of their five-fold rotation axes and arranged parallel to the crystallographic c axis. The C and Al atoms are accommodated in two types of channels parallel to these bars. In one type the C1, C2, Al2, and Al3 atoms alternatingly occupy tetrahedrally surrounded sites (C1 and C2 sites with the vertices, and Al2 and Al3 sites with the faces of the adjacent icosahedra forming the corners of the tetrahedra). The Al1 sites in the other type of channels are nearly octahedral cavities formed by two edges and four vertices of the adjacent icosahedra like copper in $B_{25}AlCu$ (3). The minimum distance between the Al1 atoms and the short Al1–B distances are responsible for the symmetry reduction to the orthorhombic structure. The Al1 and the disordered Al2 and Al3 sites are occupied as follows: Al1, 0.445(3); Al2(A), 0.314(3); Al2(B), 0.151(3); Al3(A), 0.312(3); Al3(B), 0.169(3).

Assuming that the four valence electrons of the single C atoms saturate the intericosahedral covalent bonds of the adjacent B atoms, the electron deficiency of two electrons per icosahedron is satisfactorily compensated, if a threefold ionization of the 2.80(1) Al atoms per formula unit is assumed (1). However, the assumption of a threefold ionization of the Al atoms seems rather improbable and is not compatible with the rather weak phonon bands indicating low ionicity, and therefore in accordance with the quantitative compensation of the electron deficiency in β-rhombohedral boron and boron carbide (4) an immediate correlation between electronic s-tructure and structural defects may exist, whose verification requires electronic band structure calculations of the idealized structure. In the present investigation this assumption is qualitatively supported by gap-state-related transitions in the optical absorption (see below).

For results of previous investigations on $B_{48}Al_3C_2$ see (5,9) and references therein; for optical measurements see also (6) and references therein.

SAMPLE MATERIAL

The orthorhombic, partly intergrown crystals (space group $\acute{I}m2b$, No. 46) with sizes up to about 12 mm were prepared with the metal–solution technique at 1380°C (15 h) (for details see (1)). The lattice parameters are $a = 12.390(3)$ Å, $b = 12.637(3)$ Å, and $c = 10.136(4)$ Å. The plane-parallel samples for optical transmission measurements were cut from the crystalline lumps, grounded to suitable thicknesses, and polished with diamond (final grain

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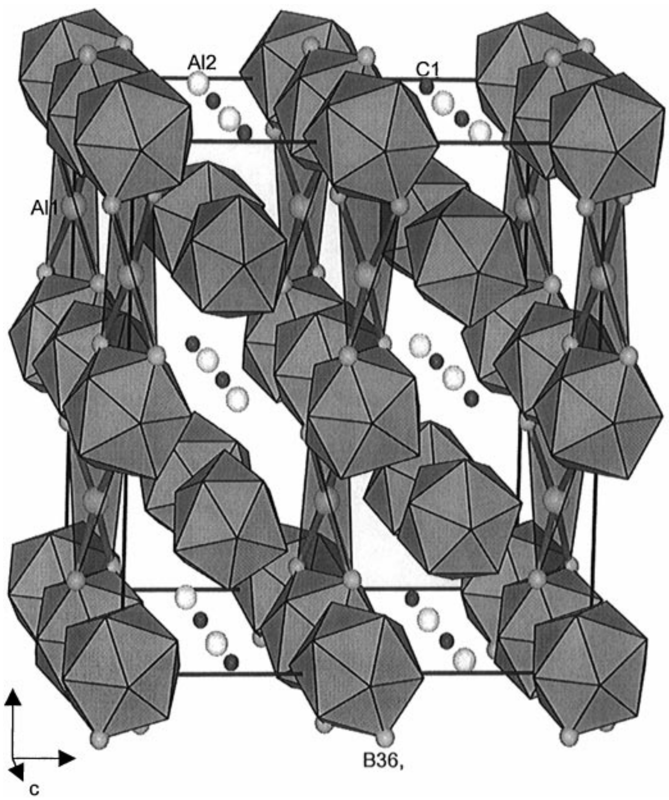

FIG. 1. Crystal structure of $B_{48}Al_3C_2$ with four symmetry-independent B_{12} icosahedra. The tetrahedral coordination of the Al1 atoms is the reason for the orthorhombic distortion (1).

size 1 μm). They were transparent and exhibit an amber-like color. The samples were not crystallographically orientated, and therefore, because of the anisotropy, the properties depend somewhat on the individual sample.

RESULTS

Absorption Edge

For interband transitions of electrons between parabolic bands the following dependencies are theoretically expected [see (7)]:

- For direct-allowed transitions: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g)^{1/2}$
- for direct-forbidden transitions: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g)^{3/2}$
- for indirect-allowed transitions with phonon emission: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g - \hbar\Omega_{\text{phonon}})^2$
- for indirect-allowed transitions with phonon absorption: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g + \hbar\Omega_{\text{phonon}})^2$
- for indirect-forbidden transitions with phonon emission: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g - \hbar\Omega_{\text{phonon}})^3$
- for indirect-forbidden transitions with phonon absorption: $\alpha(\hbar\omega) \propto (\hbar\omega - E_g + \hbar\Omega_{\text{phonon}})^3$.

Nondirect transitions between electronic levels consisting of localized states occurring, for example, in the energy band tails of amorphous semiconductors exhibit the same energy dependence of the absorption coefficient like indirect-allowed transitions, and therefore they cannot be distinguished from them by this method only.

According to Lucovsky (8), for the transition of electrons from a deep level with the ionization energy E_I, which is assumed to have a delta-function-like density of states distribution, into a parabolic band, one expects

$$\alpha(\hbar\omega) \propto E_I^{1/2}(\hbar\omega - E_I)^{3/2}/(\hbar\omega)^3.$$

For the Urbach tail of an absorption edge, occurring in cases where the densities of states exponentially decrease toward the gap, the absorption coefficient is expected to vary exponentially depending on photon energy.

To determine the kind of transition, the experimental results are plotted vs photon energy in a suitably modified relation (for example, for direct-allowed transitions $(\alpha(\hbar\omega))^2$ vs $(\hbar\omega)$), so that a linear slope occurs if the particular theory is fulfilled. The extrapolation of this linear slope to zero yields the optical transition energy. The extrapolation to higher energies describes the high-energy behavior of this transition and therefore makes it possible to subtract this transition from the total absorption coefficient measured, and then to proceed with the decomposition of the absorption edge by determining the next transition as described.

The absorption spectra in the absorption edge range of two different samples are displayed in Fig. 2. The difference indicates the optical anisotropy because the samples were arbitrarily cut from the lumps and not crystallographically orientated. The absorption edges were decomposed step by step using a local program that makes it possible to easily fit the different theories of interband transitions (see (7)), localized level-to-band transitons (8), and Urbach tails to the experimental data. The character of the best fit was attributed to the transition; the results are listed in Table 1.

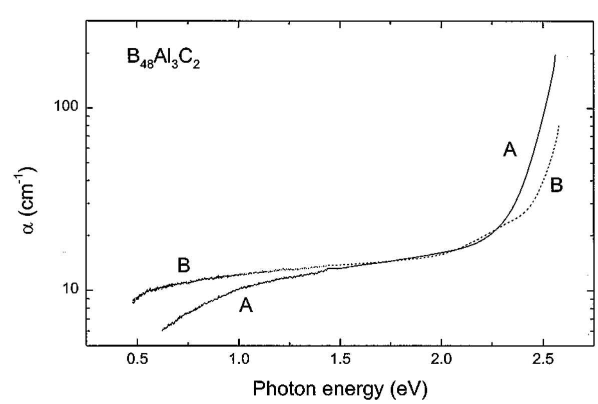

FIG. 2. Optical absorption spectra of $B_{48}Al_3C_2$ in the spectral range of interband and gap-state-related transitions. The difference of the spectra is due to the optical anisotrophy of samples arbitrarily cut from single crystals.

TABLE 1
Optical Transition Energies Determined from Spectra A and B (Different Individuals) Samples in Fig. 1

	$\hbar\omega$ (eV)		
No.	Sample A	Sample B	Characterization
1	0.45		Deep level
2		0.60	Deep level
3	0.78	0.76	Deep level
4		0.96	Deep level
5	0.97	1.03	Indirect allowed or nondirect
6	2.06	1.91	Indirect allowed or nondirect
7	2.10		Indirect allowed or nondirect
8	2.26		Indirect allowed or nondirect
9	2.34		Indirect allowed or nondirect
10	2.40	2.38	Indirect allowed or nondirect
11	2.45	2.44	Indirect allowed or nondirect
12	2.50	2.50	Indirect allowed or nondirect

The less-detailed transition energies determined in (9) are largely confirmed.

OPTICAL PHONONS

The IR absorbance and the Raman spectra (1) are displayed in Fig. 3, and the resonance frequencies are listed in Table 2.

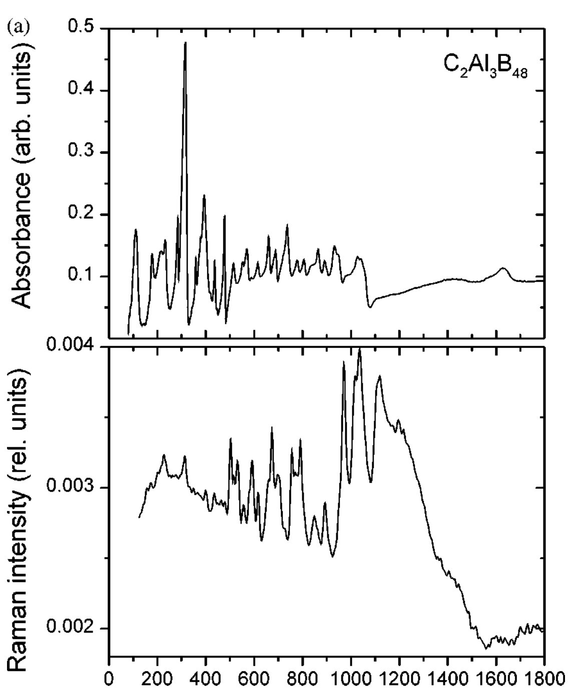

FIG. 3. Phonon spectra of $B_{48}Al_3C_2$. (a) Absorbance A, calculated from the optical transmission τ according to $A = ln\,(1/\tau)$. The influence of the reflectivity was neglected and the light scattering roughly eliminated by an empirical estimation. Spectral resolution was 2 cm^{-1}. (b) Raman intensity vs wavenumbers. Spectral resolution was 4 cm^{-1}.

TABLE 2
Phonon Frequencies of $B_{48}Al_3C_2$

No.	IR	Raman
1	1633	
2	1580(5)	
3	1400–1460	1400–1460
4		1236
5		1216
6		1196
7		1174
8		1147
9		1119
10		1108
11	1058	
12	1042	1036
13	1027	
14		1017
15	982	
16		971
17	948	
18	933	
19	892	893
20	865	861
21		849
22	836	
23	806	
24		791
25	778	769
26		756
27	737	
28	725	726
29	689	697
30		673
31	660	660
32	615	616
33	589	592
34	570	580
35	563	556
36		531
37	515	516
38		503
39	477	480
40		464
41		449
42	437	435
43	420	
44	393	400
45	379	
46	359	365
47		349
48		334
49	316	314
50	285	294
51	278	276
52		264
53		252
54	233	237
55		227
56	214	215
57		201
58	179	173
59		156
60	111	114
61	105	

The completely occupied idealized orthorhombic unit cell (four units of $B_{48}Al_5C_2$) consists of 220 atoms, 110 of which belong to the primitive cell. Accordingly the total number of phonons is 327. There are 252 IR-active modes (88 A_1, 75 B_1, 89 B_2) and 327 Raman-active modes (88 A_1, 75 A_2, 75 B_1, 89 B_2) expected. The A_1, B_1, and B_2 are both IR- and Raman-active. This is not in accordance with the measured spectra, where roughly only one-third of the phonons have both activities. This suggests taking the α-tetragonal structure of the HT phase of $B_{48}Al_3C_2$ with 56 atoms per unit cell into consideration, where Al1 occupies a fourfold site by 25%. That structure only weakly deviates from the real orthorhombic description. According to group theory, 62 IR-active (23 B_2 and 39 E) modes and 98 Raman-active (20 A_1, 16 B_1, 23 B_2, and 39 E) modes are expected (6). The E modes are IR- and Raman-active as well. Their relative share (39 of 121) corresponds to the measured spectrum. Indeed, the number of experimentally determined phonons is much lower; however, group theory does not give information on intensity and accidental degeneracy. But apparently the expected frequency splitting in consequence of the lattice distortion to the real orthorhombic structure is below the resolution of the measured spectra.

From other icosahedral boron-rich solids it is known that the icosahedral vibrations are found between about 400 and 1100 cm^{-1} (see (5)). At frequencies $> 1000\ cm^{-1}$ usually the valence vibrations (stretching modes) of single atoms occur. In the present spectrum a reliable attribution of the high-frequency phonons is not possible; impurity atoms cannot definitely be excluded. Since in $B_{48}Al_3C_2$ there are no bigger structural units than B_{12} icosahedra, for frequencies $< 400\ cm^{-1}$ the bending modes of the single atoms are expected to determine the phonon spectrum.

The Al1 atom is nearly tetrahedrally bonded between each two B atoms of both adjacent icosahedra (see Fig. 1). This bonding is similar to that in XY_4 molecules. As discussed in detail by Herzberg (10), such molecules have four normal vibrations separated in groups of two at high and two at low frequencies, respectively. The relation between the average frequencies of both groups varies between about 2 for light to about 4 for heavy Y atoms. Therefore it seems possible to attribute the double bands at 1633/1580 cm^{-1} and 316/285 cm^{-1} in the IR spectrum to the vibrations of the Al1 atom. However, these vibrations should be Raman active as well, and there are no clear indications of the high-frequency vibrations in the measured Raman spectrum.

Polarization-dependent investigations on single crystals and on other compounds with the same structure may give a better basis for interpreting the phonon spectrum.

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