# Interband Transitions and Optical Phonons of B<sub>48</sub>Al<sub>3</sub>C<sub>2</sub>

H. Werheit and R. Schmechel<sup>1</sup>

Solid State Physics Laboratory, Gerhard-Mercator University, D-47048 Duisburg, Germany

and

## F. D. Meyer and H. Hillebrecht

Department ACI, University of Bayreuth, Universitätsstrasse 30, D-95447 Bayreuth, Germany

Received September 9, 1999; in revised form January 21, 2000; accepted January 30, 2000

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 B48Al3C2 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  $\alpha$ -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 A12 and Al3 sites with the faces of the adjacent icosahedra forming the corners of the tetrahedra). The All 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  $\beta$ -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 Im2b, 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



<sup>&</sup>lt;sup>1</sup>Present address: Darmstadt University of Technology, Material Science, Deptartment of Electronic Materials, D-64287 Darmstadt, Germany.



FIG. 1. Crystal structure of B48Al3C2 with four symmetry-independent  $B_{12}$  icosahedra. The tetrahedral coordination of the All 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:  $\alpha(\hbar\omega) \propto (\hbar\omega \tilde{E}_{o})^{3/2}$

• for indirect-allowed transitions with phonon emission:  $lpha(\hbar\omega) \propto (\hbar\omega - E_{\rm g} - \hbar\Omega_{\rm phonon})^2$ 

• for indirect-allowed transitions with phonon absorption:  $\alpha(\hbar\omega) \propto (\hbar\omega - E_{\rm g} + \hbar\Omega_{\rm phonon})^2$ • for indirect-forbidden transitions with phonon emis-

sion:  $\alpha(\hbar\omega) \propto (\hbar\omega - E_{\rm g} - \hbar\Omega_{\rm phonon})^3$ • for indirect-forbidden transitions with phonon absorption:  $\alpha(\hbar\omega) \propto (\hbar\omega - E_{\rm g} + \hbar\Omega_{\rm phonon})^3$ .

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  $E_{\rm I}$ , which is assumed to have a delta-function-like density of states distribution, into a parabolic band, one expects

$$\alpha(\hbar\omega) \propto E_{\rm I}^{1/2}(\hbar\omega - E_{\rm I})^{3/2}/(\hbar\omega)^3$$

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

TABLE 2Phonon Frequencies of B48Al3C2

	$\hbar\omega$ (eV)			
No.	Sample A Sampl		3 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  $\tau$  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  $2 \text{ cm}^{-1}$ . (b) Raman intensity vs wavenumbers. Spectral resolution was  $4 \text{ cm}^{-1}$ .

1         1633           2         1580(5)           3         1400-1460           4         1236           5         1216           6         1196           7         1174           8         1147           9         1119           10         108           11         1058           12         1042           13         1027           14         1017           15         982           16         971           17         948           18         933           19         892         893           20         865         861           21         849         22           23         806         24           791         25         778           26         733         769           26         733         660           31         660         660           32         615         616           33         589         592           34         570         580           35         563	No.	IR	Raman
21580(5)31400-14601400-1460412365121661196711748114791191011081110581210421310271410171598216971179481893319892208658612183623806247912572629689660660316606606603261561653335893947744393404644144942437434204439345359365356365153751536316316314502852944433945277562142152565423335525254233359365562143593655621421525656214215566572505817959156 <tr< td=""><td>1</td><td>1633</td><td></td></tr<>	1	1633	
31400-14601400-146041236512166119671174811479111910108111058121042131027140117159821697117948189331989228938932086586586121849228362380624791257787787692675627737287252968969730316605261556355636516375155163939477480304443934046441449424374342044393453794635936526551278262765226433324434204439345379463593652145155165226453252542335520155 <t< td=""><td>2</td><td>1580(5)</td><td></td></t<>	2	1580(5)	
4       1236         5       1216         6       1196         7       1174         8       1147         9       1119         10       1008         11       1058         12       1042         13       1027         14       017         15       982         16       971         17       948         18       933         19       892       893         20       865       861         21       836       23         22       836       23         23       806       24         791       25       778         25       778       769         26       755       726         27       737       28         28       725       726         29       689       697         31       660       660         32       615       616         33       589       592         34       570       580         35       563       556	3	1400-1460	1400-1460
5       1216         6       1196         7       1174         8       1147         9       110         10       1108         11       1058         12       1042       1036         13       1027         14       0117         15       982         16       971         17       948         18       933         19       892         20       865         21       849         22       836         23       806         24       791         25       778         769       76         26       756         27       737         28       725         29       689         660       660         31       660         32       615         33       589         35       563         36       503         37       515         38       503         39       477         44       399	4		1236
6       1196         7       1174         8       1147         9       1119         10       1008         11       1058         12       1042       1036         13       1027         14       1017         15       982         16       971         17       948         18       933         19       892         20       865         21       849         22       836         23       806         24       791         25       778         769       76         27       737         28       725         29       689         660       660         31       660         32       615         33       589         34       570         35       563         36       515         37       515         38       30         40       444         433       420         444       393	5		1216
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6		1196
8       1147         9       1119         10       1108         11       1058         12       1042         13       1027         14       1017         15       982         16       971         17       948         18       933         19       892         20       855         21       849         22       836         21       849         22       836         23       806         24       791         25       778         769       76         27       737         28       725         29       689         660       660         31       660         32       615         615       616         33       589         592       54         34       570         35       563         36       503         37       515         38       503         39       477	7		1174
9       1119         10       108         11       105         12       1042       1036         13       1027       1017         15       982       982         16       971       948         18       933       933         19       892       893         20       865       861         21       849       849         22       836       23         806       791       25         27       737       756         28       725       726         29       689       697         30       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       531       516         38       503       556         39       477       480         40       449       449         42       437       435         43       420       444         449       344       349 </td <td>8</td> <td></td> <td>1147</td>	8		1147
10       1108         11       1058         12       1042       1036         13       1027       1017         14       982       1017         15       982       971         16       971       948         18       933       933         19       892       893         20       865       861         21       849       849         22       836       23         23       806       24         24       791       25         25       778       769         26       756       726         29       689       697         30       673       516         31       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       531       516         38       503       516         39       477       480         44       393       400         45       379 </td <td>9</td> <td></td> <td>1119</td>	9		1119
11       1058         12       1042       1036         13       1027       1         14       1017       15         15       982       1         16       971       1         17       948       1         18       933       1         19       892       893         20       865       861         21       849       2         23       806       2         24       791       25         25       778       769         26       755       726         27       737       2         28       725       726         29       689       697         30       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       531       515         37       515       516         38       503       355         39       477       480         441       44	10		1108
12 $1042$ $1036$ 13 $1027$ 14 $1017$ 15 $982$ 16 $971$ 17 $948$ 18 $933$ 19 $892$ 20 $865$ 21 $849$ 22 $836$ 23 $806$ 24 $791$ 25 $778$ $769$ 26 $756$ 27 $737$ $726$ 29 $689$ $697$ 30 $673$ $616$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ 36 $503$ $595$ 39 $477$ $480$ 40 $449$ $449$ 42 $437$ $435$ 43 $420$ $4449$ 44 $393$ $400$	11	1058	
13 $1027$ 14 $1017$ 15 $982$ 16 $971$ 17 $948$ 18 $933$ 19 $892$ $893$ 20 $865$ $861$ 21 $849$ $849$ 22 $836$ $23$ 23 $806$ $24$ 24 $791$ $756$ 27 $737$ $786$ 28 $725$ $726$ 29 $689$ $697$ 30 $673$ $616$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ 36 $531$ $576$ 37 $515$ $516$ 38 $503$ $592$ 344 $393$ $400$ 45 $379$ $76$ 46 $359$ $365$ 47	12	1042	1036
14 $1017$ 15       982         16       971         17       948         18       933         19       892       893         20       865       861         21       849       849         22       836       861         23       806       701         24       791       756         27       737       737         28       725       726         29       689       697         30       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       531       576         37       515       516         38       503       556         36       531       576         37       515       516         38       503       556         39       477       480         40       449       420         41       439       440         42 <td>13</td> <td>1027</td> <td></td>	13	1027	
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 $737$ $726$ 28 $725$ $726$ 29 $689$ $697$ 30 $673$ $616$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ 36 $503$ $591$ 37 $515$ $516$ 38 $503$ $563$ 39 $477$ $480$ 44 $933$ $400$ 45 $379$ $65$ 47 $393$ $264$	14	222	1017
16 $9/1$ $17$ $948$ $18$ $933$ $19$ $892$ $893$ $20$ $865$ $861$ $21$ $836$ $23$ $806$ $24$ $791$ $25$ $778$ $769$ $26$ $756$ $27$ $737$ $28$ $725$ $726$ $29$ $689$ $697$ $30$ $673$ $31$ $660$ $660$ $32$ $615$ $616$ $33$ $589$ $592$ $34$ $570$ $580$ $35$ $563$ $556$ $36$ $515$ $516$ $38$ $503$ $393$ $477$ $480$ $40$ $444$ $414$ $449$ $42$ $437$ $435$ $43$ $420$ $444$ $449$ $316$ $314$ $50$ $285$ $294$ $45$ $379$ $276$ $52$ $264$ $233$ $51$ $277$ $56$ $214$ $215$ $57$ $201$ $58$ $179$ $173$ $59$ $156$ $60$ $111$ $114$ $114$	15	982	071
17       948         18       933         19       892       893         20       865       861         21       849       849         22       836       849         23       806       701         24       791       737         25       778       769         26       756       727         27       737       737         28       725       726         29       689       697         30       673       615         31       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       515       516         38       503       563         39       477       480         40       449       449         42       437       435         43       420       444         44       393       400         45       379       276         52       264 <td>16</td> <td>0.48</td> <td>9/1</td>	16	0.48	9/1
18       935         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       616         32       615       616         33       589       592         34       570       580         35       563       556         36       515       516         37       515       516         38       503       59         39       477       480         40       433       420         44       393       400         45       379       46         46       314       34         49       316       314         50       285       294         51       278       276         52       233       237	1/	948	
19 $892$ $893$ 20 $865$ $861$ 21 $849$ 22 $836$ 23 $806$ 24 $791$ 25 $778$ $769$ 26 $756$ 27 $737$ $725$ 28 $725$ $726$ 29 $689$ $697$ 30 $673$ $616$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ 36 $531$ $515$ 37 $515$ $516$ 38 $90$ $477$ $480$ 40 $437$ $435$ 44 $393$ $400$ 45 $379$ $316$ 46 $359$ $365$ 47 $285$ $294$ 51 $278$ $276$ 52 $264$ $233$ <	10	933	202
20 $803$ $801$ 21 $849$ 22 $836$ 23 $806$ 24 $791$ 25 $778$ $769$ 26 $756$ 27 $737$ 28 $725$ $726$ 29 $689$ $697$ 30 $673$ $616$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ $36$ $511$ $516$ $37$ $515$ $516$ $38$ $503$ $503$ $39$ $477$ $480$ $41$ $449$ $435$ $42$ $437$ $435$ $44$ $393$ $400$ $45$ $379$ $365$ $47$ $825$ $294$ $51$ $278$ $276$ $52$ $264$ $233$ $237$	19	892	895 961
22 $836$ 23 $806$ 24       791         25 $778$ $769$ 26       756         27 $737$ 28 $725$ $726$ 29 $689$ $697$ 30 $673$ $615$ 31 $660$ $660$ 32 $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $556$ 36 $503$ $556$ 37 $515$ $516$ 38 $503$ $593$ 39 $477$ $480$ 40 $464$ $449$ 41 $449$ $449$ 42 $437$ $435$ 43 $420$ $314$ 44 $393$ $400$ 45 $379$ $66$ 47 $349$ $344$ 49 $316$ $314$ 50 $285$ $294$	20	805	840
23       806         24       791         25       778       769         26       756         27       737         28       725       726         29       689       697         30       673       673         31       660       660         32       615       616         33       589       592         34       570       580         35       563       556         36       515       516         38       503       556         39       477       480         40       449       420         41       449       435         43       420       444         44       393       400         45       379       46       359       365         47       349       316       314         50       285       294       51       276         51       278       276       25       264         53       252       264       233       237         54       233       237	21	836	049
24       791 $25$ 778       769 $26$ 756 $27$ 737 $28$ 725       726 $29$ 689       697 $30$ 673       616 $31$ 660       660 $32$ 615       616 $33$ 589       592 $34$ 570       580 $35$ 563       556 $36$ 515       516 $36$ 503       356 $37$ 515       516 $38$ 503       355 $39$ 477       480 $40$ 449       449 $42$ 437       435 $43$ 420       444 $44$ 393       400 $45$ 379       349 $48$ 334       420 $44$ 393       276 $52$ 278       276 $52$ 264       233       237 $55$ 214       215	22	806	
25 $778$ $769$ $26$ $756$ $27$ $737$ $28$ $725$ $726$ $29$ $689$ $697$ $30$ $673$ $615$ $31$ $660$ $660$ $32$ $615$ $616$ $33$ $589$ $592$ $34$ $570$ $580$ $35$ $563$ $556$ $36$ $531$ $515$ $37$ $515$ $516$ $38$ $503$ $535$ $39$ $477$ $480$ $400$ $464$ $444$ $41$ $449$ $420$ $44$ $393$ $400$ $45$ $379$ $349$ $48$ $334$ $490$ $48$ $327$ $276$ $52$ $278$ $276$ $54$ $233$ $237$ $55$ $227$ $56$ $54$ $233$ $237$ $55$ $227$	23	800	791
26 $756$ $27$ $737$ $28$ $725$ $726$ $29$ $689$ $697$ $30$ $673$ $613$ $31$ $660$ $660$ $32$ $615$ $616$ $33$ $589$ $592$ $34$ $570$ $580$ $35$ $563$ $556$ $36$ $515$ $516$ $38$ $503$ $503$ $39$ $477$ $480$ $40$ $464$ $411$ $449$ $42$ $437$ $435$ $433$ $420$ $444$ $393$ $44$ $393$ $400$ $45$ $379$ $46$ $314$ $49$ $316$ $314$ $50$ $285$ $294$ $51$ $278$ $276$ $52$ $264$ $233$ $237$ $55$ $227$ $56$ $214$ $215$ $57$ $201$ $56$ $60$ <td>25</td> <td>778</td> <td>769</td>	25	778	769
737 $737$ $28$ $725$ $726$ $29$ $689$ $697$ $30$ $673$ $31$ $660$ $660$ $32$ $615$ $616$ $33$ $589$ $592$ $34$ $570$ $580$ $35$ $563$ $556$ $36$ $531$ $516$ $38$ $503$ $503$ $39$ $477$ $480$ $40$ $464$ $411$ $44$ $393$ $400$ $45$ $379$ $466$ $45$ $379$ $466$ $44$ $393$ $400$ $45$ $379$ $466$ $47$ $349$ $316$ $48$ $334$ $39$ $49$ $316$ $314$ $50$ $285$ $294$ $51$ $278$ $276$ $52$ $201$ $55$ $57$ $201$ $58$ $57$ $201$	26	110	756
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       516         37       515       516         38       503       59         39       477       480         40       464       449         41       449       42         43       420       437       435         44       393       400       464         41       449       449       449         42       437       345       43         44       393       400       444         45       379       46       359       365         47       349       316       314       50       285       294         51       278       276       252       264       233       237       55       227       56       214       215       57       201	27	737	
29 $689$ $697$ 30 $673$ 31 $660$ 32 $615$ $615$ $616$ 33 $589$ $592$ 34 $570$ $580$ 35 $563$ $56$ 36 $531$ $37$ $515$ $516$ $38$ $503$ $39$ $477$ $480$ $40$ $464$ $41$ $449$ $42$ $437$ $43$ $420$ $44$ $393$ $400$ $316$ $45$ $379$ $46$ $359$ $365$ $274$ $48$ $334$ $49$ $316$ $51$ $278$ $276$ $227$ $56$ $214$ $233$ $237$ $55$ $227$ $56$ $214$ $215$ $201$ $58$ $179$ $173$ $56$ $60$ $111$ $114$ $61$ $105$	28	725	726
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	29	689	697
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30		673
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	31	660	660
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32	615	616
34 $570$ $580$ $35$ $563$ $556$ $36$ $531$ $37$ $515$ $516$ $38$ $503$ $39$ $477$ $480$ $40$ $464$ $41$ $449$ $42$ $437$ $435$ $43$ $420$ $400$ $44$ $393$ $400$ $45$ $379$ $466$ $359$ $365$ $47$ $349$ $48$ $334$ $49$ $316$ $314$ $50$ $285$ $294$ $51$ $278$ $276$ $52$ $264$ $53$ $252$ $54$ $233$ $237$ $55$ $227$ $56$ $214$ $215$ $57$ $201$ $58$ $179$ $173$ $59$ $156$ $60$ $111$ $114$	33	589	592
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	34	570	580
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35	563	556
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	36		531
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	37	515	516
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	38		503
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	39	477	480
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40		464
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	41	127	449
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	42	437	435
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	43	420	400
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	44	370	400
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	46	359	365
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40	557	349
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	48		334
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	49	316	314
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	50	285	294
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	51	278	276
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	52		264
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	53		252
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	54	233	237
56     214     215       57     201       58     179     173       59     156       60     111     114       61     105	55		227
57     201       58     179     173       59     156       60     111     114       61     105	56	214	215
58     179     173       59     156       60     111     114       61     105	57		201
59     156       60     111     114       61     105	58	179	173
60         111         114           61         105         105	59		156
61 105	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<sub>1</sub>, 75 B<sub>1</sub>, 89 B<sub>2</sub>) and 327 Raman-active modes (88 A<sub>1</sub>, 75 A<sub>2</sub>, 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 B48Al3C2 with 56 atoms per unit cell into consideration, where All 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<sub>2</sub> 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  $1100 \text{ cm}^{-1}$  (see (5)). At frequencies > 1000 cm<sup>-1</sup> usually the valence vibrations (stretching modes) of single atoms occur. In the present spectrum a reliable attribution of the highfrequency phonons is not possible; impurity atoms cannot definitely be excluded. Since in B<sub>48</sub>Al<sub>3</sub>C<sub>2</sub> there are no bigger structural units than B<sub>12</sub> icosahedra, for frequencies < 400 cm<sup>-1</sup> the bending modes of the single atoms are expected to determine the phonon spectrum.

The All 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<sup>-1</sup> and 316/285 cm<sup>-1</sup> 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.

#### REFERENCES

- F. D. Meyer, Thesis, Albert-Ludwigs University, Freiburg, Germany, 1998.
- 2. F. D. Meyer and H. Hillebrecht, in preparation.
- 3. I. Higashi and Y. Takahashi, J. Less-Common Met. 108, 177 (1985).
- R. Schmechel and H. Werheit, J. Phys.: Condens. Matter 11, 6803 (1999).
- H. Werheit, *In* "Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Group III Condensed Matter," Vol. 41D. Springer-Verlag, Berlin, 2000, p. 1.
- 6. H. Werheit, Prog. Cryst. Growth Charact. 16, 179 (1988).
- 7. R. A. Smith, "Wave Mechanics in Crystalline Solids." Chapman & Hall, London, 1961.
- 8. G. Lucovsky, Solid State Commun. 3, 299(1965).
- H. Haupt, H. Werheit, V. Siejak, V. N. Gurin, and M. M. Korsukova, *In* "Proceedings 9th International Symposium on Boron, Borides and Related Compounds, University of Duisburg, Duisberg, Germany, Sept. 21–25, 1987." (H. Werheit, Ed.), p. 387.
- G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," p. 165. Van Nostrand Reinhold, New York, 1945.