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Interaction of Optically Excited Carriers with Intraicosahedral Phonons

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The transport of electrons in boron-rich solids is strongly impeded by capture processes in intrinsic traps. For β-rhombohedral boron it was shown that these traps are generated by the interaction between electrons and specific intraicosahedral phonons. The phonons involved are quenched, when the traps are occupied by doping with suitable metals leading to *n*-type. To prove this phonon quenching, in β-rhombohedral boron and boron carbide electron–hole pairs have been generated by optical interband excitation. For optical steady-state excitation the existence of band-type carriers is proved by a Drude-type free-carrier absorption. Difference spectra of optically excited and unexited samples confirm that the phonons, which interact with electrons to generate the traps, are quenched at a measurable degree. A misinterpretion caused by the temperature raised by the irradiation can definitely be excluded, because this effect would be opposite to the one measured.

INTRODUCTION

Electron–phonon interaction is an essential phenomenon in icosahedral boron-rich solids (1–4). The icosahedra beeing the essential structural elements in the variaty of structures ranging from α-rhombohedral boron with 12 to YB_{66} with more than 1600 atoms per unit cell are not regular but distorted in consequence of the static Jahn–Teller effect. This has a strong effect on the electronic properties as well: The electronic orbitals of the icosahedra split and occupied and unoccupied orbitals are separated. This is the reason that icosahedral boron-rich solids are semiconductors in spite of the odd number of electrons of the boron atom. The *p*-type conductivity, which is an additional common property of the boron-rich solids, has its origin in high density intrinsic trapping levels. They are generated by an electron–phonon interaction between free electrons and specific intraicosahedral phonons.

The incorporation of specific intraicosahedral phonons has been proved in β-rhombohedral boron by quenching of these phonons, when the intrinsic traps become occupied in the case of interstitial doping with Fe (5) and V atoms (6), leading to *n*-type. Obviously the donor levels of these metal atoms in β-rhombohedral boron are close to the conduction band edge, and therefore the electrons transferred to the boron structure occupy the trapping levels, which are at energetically lower positions.

The aim of the present work was to check whether this phonon quenching occurs in the same way when electrons originating from optical interband excitations are subsequently trapped. An additional question to be answered is, whether similar effects are present in boron carbide, which is assumed to be closely related to β-rhombohedral boron with respect to the electronic properties.

EXPERIMENTAL

The measurements were performed with a FTIR spectrometer (Model 113v, Bruker, Karlsruhe). For optical excitation a GaAlAs laser diode (827 nm = 1.50 eV; intensity, 30 mW) was used, whose beam was collimated to 0.10(1) mrad. The beam was directly led to the sample from a distance of about 30 cm.

To realize reproducible starting conditions for the measurements, the samples were first kept for 40 h at room temperature in the cryostat of the spectrometer. For the spectra with optical excitation the samples were exposed to the excitation by the laser diode for the whole time; for the reference spectra they were kept in complete darkness. Then the temperatures 450, 300, 100, and 80 K were set in this sequence with a cooling rate of 3 K/min in between and after waiting for 2 h each after the specific temperature was reached. The starting temperature of 450 K was chosen because it is known that at this temperature just few minutes maximum are necessary to achieve thermal equilibrium. This was confirmed by the results showing that at this temperature there was no remarkable difference of the phonon spectra with and without optical excitation. It is necessary to mention that during measurement the samples were in any case exposed to the broad band optical emission of the Globar source of the spectrometer. However, because

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of the relatively low Globar temperature (1500 K) its emission in the range of interband transitions is low.

SAMPLES

We investigated high purity single-crystal β-rhombohedral boron (Wacker, Munich; claimed purity 99.9999% apart from about 90 ppm carbon) and technical polycrystalline boron-rich boron carbide $B_{10.37}C$, which was obtained by hot-pressing and subsequent melting (H. C. Starck, Laufenburg, technical purity with O, 1100 ppm; N, 13500 ppm; Fe, 1100 ppm; Mg 10 ppm; other metals, <2400 ppm (see (7)).

The surfaces were mechanically polished with diamond (finest grade 1 μm) and in the case of β-rhombohedral boron etched with a solution of $K_3[Fe(CN)_6]$, KOH, and H_2O (8).

RESULTS AND DISCUSSION

The calculated difference spectra (excited minus unexcited) are presented in Fig. 1 for β-rhombohedral boron and Fig. 2 for $B_{10.37}C$. The intraicosahedral phonons, which are known to be incorporated in the formation of intrinsic traps in β-rhombohedral boron are those at 476 and 982 cm^{-1} (symmetry type A_{2u}) and 478 and 984 cm^{-1} (symmetry type E_u) (3, 9). They are due to antisymmetric breathing modes of the icosahedron described by a contracting upper and expanding lower pentagon of the free icosahedron (F_{1u}) and an oblate and a prolate hemispheroid (F_{2u}), respectively (10). The corresponding phonons in boron carbide are those at 416 cm^{-1} (A_{2u} and E_u) and 1064 (E_u) (11). At higher frequencies there are strong nonicosahedral phonons (1245 cm^{-1} for β-rhombohedral boron and 1534 cm^{-1} for boron carbide, symmetry type A_{2u} of both) belonging to the vibration of the central single B atom in the unit cell of β-rhombohedral boron and to the stretching mode of the three-atomic chain in boron carbide, respectively.

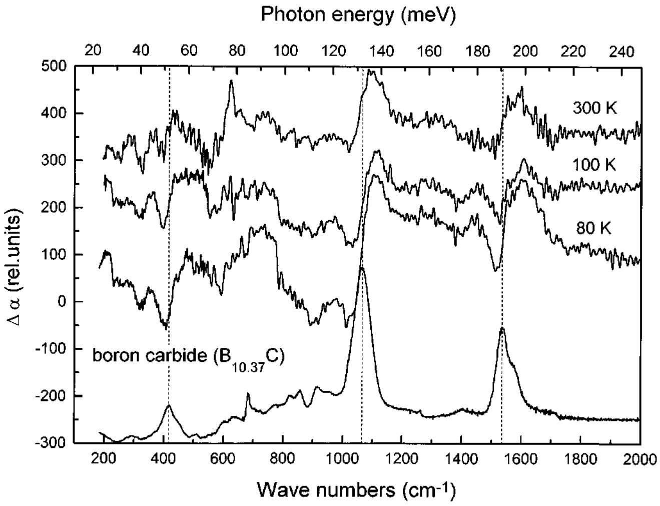

FIG. 2. Boron-rich boron carbide ($B_{10.37}C$). Difference of the IR phonon spectra with and without optical excitation 80, 100, and 300 K. Bottom tracing, phonon spectrum boron carbide for orientation.

The change of the oscillator strengths of the stronger phonons in β-rhombohedral boron depending on temperature are shown in Fig. 3. The quenching of both phonons in consequence of the optical excitation is obvious. The increase of phonon quenching with increasing temperature can be easily explained by the probability of trap generation. It increases with the thermal excitation of phonons, which are needed for the electron–phonon interaction. The oscillator strengths of the 1245 cm^{-1} phonon decreases as

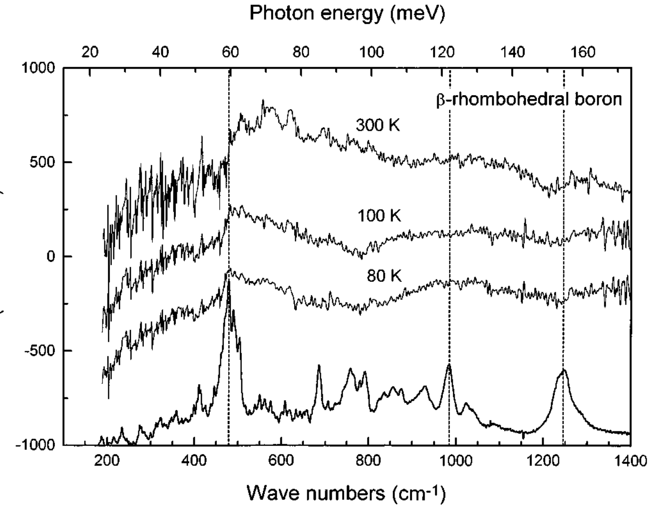

FIG. 1. β-Rhombohedral boron. Differences of the IR phonon spectra with and without optical excitation at 80, 100, and 300 K. Bottom tracing, phonon spectrum of β-rhombohedral boron for orientation.

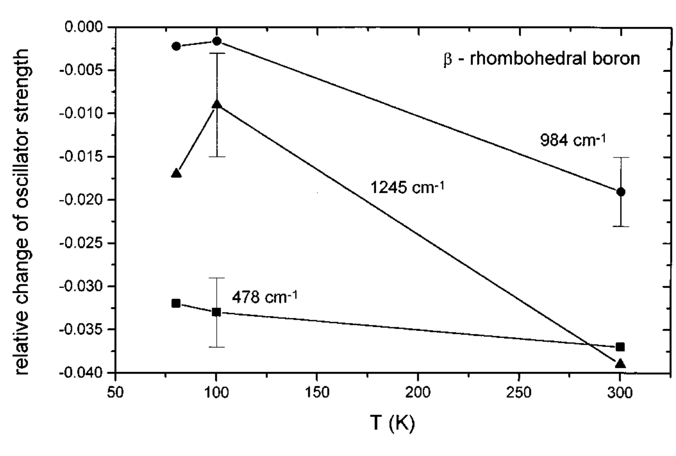

FIG. 3. β-Rhombohedral boron. Relative change of the oscillator strengths of significant phonons induced by optical excitation. 478 and 1245 cm^{-1}, intraicosahedral phonons; 1245 cm^{-1}, vibration of the central B atom.

well. This happens in the case of interstital doping as well, where as mentioned a satellite phonon band developes at lower frequencies. The effect in the case of optical excitation is too small to decide whether such a satellite phonon band developes here, too.

It should be mentioned that the optical excitation shifts the phonon resonance frequencies slightly to higher values. This shift is insignificant with respect to its value. However, its sign proves that the effect discussed is not due to an increase of temperature by the optical excitation, which would cause an opposite shift (12, 13)

There seem to be rather broad bands in the difference spectra of β-rhombohedral boron in Fig. 1 with maxima at about 100 and 500 cm^{-1} (70 and 130 meV) evoked by the optical excitation. One could imagine that in consequence of the distortion of the icosahedra by electron–phonon interaction the resonance frequencies of IR active phonons become less defined and the selection rules for Raman-active phonons are lifted, and therefore these phonons would become IR active as well. However, the density of states maxima of Raman active phonons in highly excited β-rhombohedral boron (14) and of amorphous boron with icosahedral structure (15) are at distinctly different frequencies, and therefore this explanation can be largely excluded. Probably these maxima are due to electronic transitions; however, this explanation needs further checks.

Obviously, according to Fig. 4 an electron–phonon interaction exists in boron carbide as well. However, the temperature dependence is opposite to that in β-rhombohedral boron. This can be consistently explained with the assumption that the density of occupied states at the Fermi level in boron carbide is much higher than in β-rhombohedral boron. Then in thermal equilibrium the number of traps occupied by thermal excitation of electrons from the valence band range increases with increasing temperature and accordingly the probability of trap formation after optical excitation decreases.

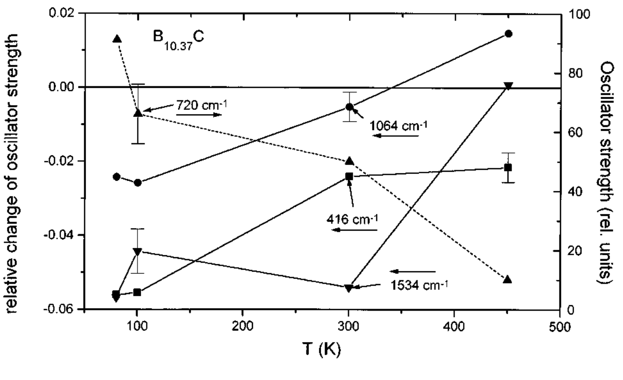

FIG. 4. $B_{10.37}C$. Relative change of the oscillator strengths of significant phonons induced by optical excitation. 416 and 1064 cm^{-1}, intraicosahedral phonons; 149 cm^{-1}, vibration of the three-atomic chain.

The oscillator strength of the 1534 cm^{-1} phonon (stretching mode of the three-atomic chain) decreases as well and exhibits the same temperature dependence like the intraicosahedral phonons. This could be due to a redistribution of charge in consequence of the optical excitation.

A new broad phonon band with center at about 720 cm^{-1} is clearly seen in the difference spectra of boron carbide in Fig. 2. Its absolute oscillator strength varies, roughly proportional to the degree of quenching of the intraicosahedral phonons (Fig. 4), and is therefore correlated with the optical excitation as well. Lifting of selection rules can be excluded because the Raman spectra of pure boron carbide do not exhibit strong phonons in this range. Probably it is a phonon, whose resonance frequency is shifted because of the change of the bond strength in icosahedra distorted by electron–phonon interaction. In β-rhombohedral boron there are intraicosahedral phonons in this spectral range, which are much clearer in Fe saturated than in pure material.

The difference of the absorption coefficients of excited and nonexcited boron carbide $\Delta\alpha$ increases toward lower photon energies, thus indicating that the dynamical conductivity increases by optical excitation (Fig. 5). The frequency dependence (roughly as ω^{-2}) seems to indicate a Drude-type conductivity, which for thermal equilibrium in this composition is found only at higher temperatures, while hopping conductivity is found in the whole range of temperature (16).

CONCLUSION

Electron–phonon interaction in connection with the formation of intrinsic traps has been confirmed for β-rhombohedral boron. Specific intraicosahedral phonons are quenched, when electrons are excited by optical interband

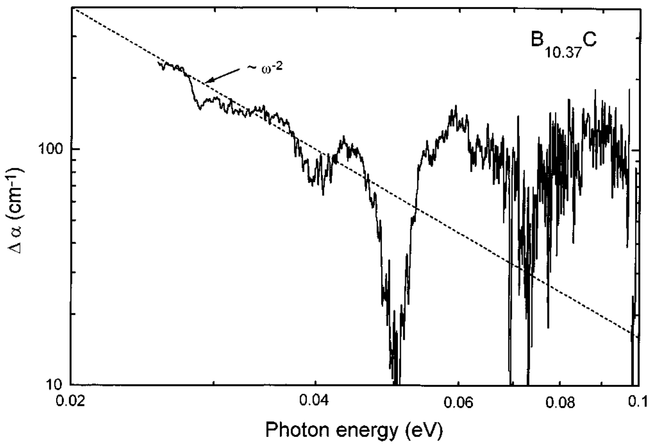

FIG. 5. $B_{10.37}C$. Low energy range of the difference spectrum of optical absorption (excited minus unexcited). Broken line, energy dependence of Drude-type carriers (phonon scattering).

transitions. This effect is qualitatively similar to that already proved in the case of *n*-doping by interstitially accommodated specific metal atoms. Similar results in the case of boron-rich boron carbide suggest related effects in this structure-related icosahedral boron-rich solid. In boron carbide the dynamical conductivity is enhanced by optical excitation.

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REFERENCES

1. R. Franz and H. Werheit, *Europhys. Lett.* **9,** 145 (1989).
2. R. Franz and H. Werheit, Influence of the Jahn–Teller effect on the electronic band structure of boron-rich solids containing B_{12} icosahedra, *in* "Boron-Rich Solids" (D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, and C. L. Beckel, Eds.), AIP Conf. Proc. 231, p. 29. Albuquerque, NM, 1990.
3. H. Werheit, On the electronic transport properties of boron carbide, *in* "The Physics and Chemistry of Carbides, Nitrides and Borides" (R. Freer, Ed.), p. 677. Kluwer, Dordrecht, 1990.
4. D. Emin, Theory of electronic and thermal transport in boron carbides, *in* "The Physics and Chemistry of Carbides, Nitrides and Borides" (R. Freer, Ed.), p. 691. Kluwer, Dordrecht, 1990.
5. H. Werheit, U. Kuhlmann, Electron–Phonon interaction in B_{12} icosahedra. *Solid State Commun.* **88,** 421 (1993).
6. R. Schmechel, H. Werheit, V. Kueffel, and T. Lundström, On the electronic properties of β-rhombohedral B:V and B:Co compounds, to appear.
7. U. Kuhlmann, H. Werheit, and K. A. Schwetz, *J. Alloys Compounds* **189,** 249 (1992).
8. H. Binnenbruck, A. Hausen, P. Runow, and H. Werheit, *Z. Naturforsch.* **25a,** 1431 (1970).
9. H. Werheit, M. Laux, and U. Kuhlmann, *Phys. Stat. Sol. B* **176,** 415 (1993).
10. C. L. Beckel and J. P. Vaughan, Vibrations of regular boron icosahedra, *in* "Boron-Rich Solids" (D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, Eds.), AIP Conf. Proc. 140, p. 305. Albuquerque, NM, 1985.
11. H. Werheit and H. Haupt, *Z. Naturforsch.* **42a,** 925 (1987).
12. J. Jaumann and H. Werheit, *Phys. Status Solidi* **33,** 587 (1969).
13. H. Binnenbruck and H. Werheit, *Z. Naturforsch.* **34a,** 787 (1979).
14. U. Kuhlmann, Thesis, University of Duisburg, 1994.
15. U. Kuhlmann, H. Werheit, T. Lundström, and W. Robers, *J. Phys. Chem. Solids* **55,** 579 (1994).
16. R. Schmechel and H. Werheit, Evidence of the superposition of Drude type and hopping type transport in boron-rich solids. *J. Solid State Chem.* **133,** 335 (1997).