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ANOMALOUS X-RAY RAMAN SPECTRUM OF POLYCRYSTALLINE BORON

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Abstract - The anomalous peaks in the x-ray Raman spectrum of polycrystalline boron have been examined experimentally and theoretically. These peaks are associated with d-like atomic states high in the conduction bands. The "anomalous" nature of these peaks is also manifested in their angular dependence.

The existence of anomalous peaks in the x-ray energy loss spectrum of Be in the region of the x-ray Raman band \([1,2]\) has motivated the search for such "anomalous" peaks in materials other than Be. These anomalous peaks are nothing more, but complex manifestations of the bonding character of the states near and above the Fermi level \([2]\). The anomalous peaks, therefore, correspond to similar peaks in the electronic density of states (DOS), around and above the Fermi level. In anticipation of discovering similar anomalous peaks in boron and thus probing its electronic structure in the unoccupied conduction bands, we undertook the present theoretical and experimental investigation for the x-ray Raman spectrum of boron.

Due to the complicated crystal structure of boron, its electronic structure is not known quite accurately. The crystal structure of boron, with several atoms per unit cell occurs in two different crystal forms, tetragonal and rhombohedral, both based on the icosahedron geometry. The simplest form, which is rhombohedral with 12 atoms per unit cell, is shown in figure 1 in a projection on the (001) plane of the unit cell. The distances are: \(a=2.03\text{Å}, \ b=1.78\text{Å}, \ c=1.73\text{Å}\) and \(d=4.91\text{Å}\) (ref.\([3]\)).
related hexagonal cell [3]. Since the basic unit for both of these complicated structures is the icosahedron, it is reasonable to model polycrystalline boron with a small cluster of 12 boron atoms in icosahedral geometry. Small cluster have been very useful and adequate in describing the anomalous peaks in the region of the x-ray Raman band of Be [2]. Needless to say that small cluster techniques can provide not only bonding information but also inner core binding energies [4] as well as structural and phonon properties [4,5]. The small atomic cluster used here to describe the electronic structure of boron consists of the twelve atoms 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 set (S.Huzinaga:Approximate wave Functions I, 1971, unpublished) and have been enhanced with virtual d-orbitals. The cluster hamiltonian is formed and diagonalized using the unrestricted Hartree-Fock (UHF) method. In the UHF, contrary to the usual restricted Hartree-Fock (RHF) method, the spin-up spin-down pairs are not restricted to have the same spatial wavefunction 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 A. Barry Kunz was employed to perform the UHF calculations.

The experimental set up for the energy loss x-ray spectroscopy underlying the x-ray Raman measurements, is similar to the one described before for Be [1]. It consists mainly of a Rigaku-Denki (type RU-200PL) 12KW 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 180mA and the spectrometer resolution was E/AE = 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 KB 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 sec.

The results of our theoretical and experimental investigations are summarized in a condensed form in fig.2, which shows the x-ray Raman spectrum and the "anomalous
The Raman band is located around 200eV and the "anomalous peaks" in the region of 380eV quite far from the Raman band. In the same figure the results of the calculation in the region of the Fermi level and the region of 300eV above the 1s level are shown in the form of an energy level diagram superimposed with the "simulated" DOS in the same energy region. This simulated DOS, as explained before \[1,6\] 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 280eV are well reproduced in the calculated energy level diagram and DOS of figure 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 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 symmetry and of different percentage of s and p admixture results in a rather large width for the corresponding "anomalous" peak. Relatively to the Raman peak, the height of the anomalous peak seems to be larger due perhaps to the more compact nature of the d orbitals, compared to the sp orbitals responsible for the Raman peak.

The spectrum of fig.2 was taken at a scattering angle of 55°, but the positions of the anomalous peaks remain practically the same for a large variety of angles. The scattering angle variation used in our x-ray Raman scattering measurements ranges from 45° to 105° with a step of 10°. The angular dependence of the intensity, only for quite low scattering angles follows the theoretical expression of Mizuno and Ohmura \[7\]. This expression based on the dipole approximation gives the scattering intensity \(I\) as a function of the scattering angle \(\varphi\)

\[
I(\varphi) = K (1+\cos^2\varphi)(\frac{4n\alpha}{\lambda_0} \sin \frac{\varphi}{2})^2
\]

(1)

where \(K\) is a constant and \(\alpha\) is the mean radius of the charge distribution of the K-electrons of the polycrystalline scatterer. Equation (1) together with the condition for the occurrence of the x-ray Raman process sets the theoretical framework for the dependence of \(I\) on \(\varphi\). The mathematical condition for the occurrence of the x-ray Raman scattering is written:

\[
\frac{4n\alpha}{\lambda} \sin \frac{\varphi}{2} \leq 1
\]

(2)

with \(\lambda\) the wavelength of the incident radiation. Equation (2) simply states that the magnitude of the momentum transfer should be smaller or equal to \(1/\alpha\) \[7\].

The observed discrepancy in the angular dependence of the spectrum for moderate and high scattering angles, based on the previous discussion (equations (1) and (2)), could be associated with a violation of the dipole approximation on which (1) is based. This assertion, is certainly in accord with our UHF cluster theoretical results which attribute the anomalous peaks to d-like atomic states. This seems to violate dipole selection rules. Certainly for a solid and in this deep in the continuum energy region, it is difficult to access the validity of dipole selection rules based on the atomistic angular momentum motion. This situation calls for a further and deeper theoretical investigation.

References