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HYBRIDIZATION EFFECTS IN SOLIDS STUDIED BY COMPTON SCATTERING

G. LOUPIAS*, J. CHOMILIER, Y. GARREAU and J. TARBES

Laboratoire de Minéralogie Cristallographie, CNRS UPMC, T 16, 4, Place Jussieu, F-75252 Paris Cedex 05, France
and 'LURE, CNRS-CEA-MEN, Bât. 209D, Université Paris-Sud, F-91405 Orsay Cedex, France

RESUME

Nous présentons une série de mesures de profils Compton sur des cristaux de LiH et de LiC₆. La comparaison avec les profils calculés permet de tester la qualité des fonctions d'onde du système, et par là de vérifier si la base de fonctions d'onde utilisées pour créer les orbitales prend en compte toutes les hybridations éventuelles.

ABSTRACT

We present a series of measurements of Compton profiles on LiH and LiC₆ crystals. The comparison with calculated profiles is a test of the quality of the wave function of the system, and it allows to check if the basis set used to develop the wave function takes care of all eventual hybridizations.

The bondings of the valence wave functions appearing in solids or molecules basically deals with the overlap of atomic wave functions, centered on two nuclei, and there is a common part of the space where both wave functions have significant values. The key problem is to find an experimental test accurate enough to evidence an overlap between nearest neighbours as small as possible. Compton profile measures, in an inelastic scattering experiment, the projection of the electron momentum density, \( n(p) \), on the scattering vector of the scattered particles:

\[
J(q) = \int n(p) \, d^2p
\]

\( q \) is the projection of \( p \) on the scattering vector;

\( n(p) \) is related to the ground state wave function \( \psi(r) \):

\[
n(p) = \chi(p) \chi^*(p)
\]

where \( \chi(p) \) is the \( p \) space wave function, Fourier transform of \( \psi(r) \).

The valence orbitals, entering in the bonds, are more contracted in momentum space, while they have a large spatial extent in \( r \) space. So, a slight modification of the electron density affects more the Compton profile than the elastic structure factor. For instance, in the case of LiF, Aikala (1)
showed that the contribution to the Compton profile due to the overlap is 10% of the total signal, while this effect is only 1% of the elastic scattering factor (2).

In this paper, we will present experimental results of inelastic scattering performed on two compounds. Firstly, a diatomic mainly ionic crystal, LiH, with few electrons involved in its configuration, can be considered as a "school case" for metallic hydrides. It will be compared with two available models. Secondly, LiC₆, which is a layered material synthesized from graphite, consisting in a succession of carbon and lithium layers, will also be compared to existing models.

1. LITHIUM HYDRIDE

The starting point for the interpretation of the electronic structure of LiH is to consider it as totally ionic: Li⁺ and H⁻. A geometrical consideration of the ionic radii, 2.08 Å for H⁻ and 0.6 Å for Li⁺, leads to an intuitive acceptance that main interactions will occur between hydrogen ions. A model more sophisticated than the ionic one will have to introduce hybridization between neighbours hydrogen ions.

Although many calculations have been performed on polycrystalline LiH, only two have been accomplished for single crystal. Aikala (2) used Li⁺ and H⁻ ionic wave functions in a MO-LCAO scheme to perform the directional Compton profile (DCP). To take care of the crystal symmetry, he used a cluster going up to the 42nd shell of neighbours (i.e. 949 ions altogether). The second model, molecular simulated crystal (MSC) (3) simulates the crystal from non-interacting LiH molecules and the total hybridized wave function of LiH takes care of 2p lithium wave functions, so it admits a partial covalence.

Figure 1 shows the difference between DCP's calculation and our experimental DCP for the scattering vector parallel to <100>. For large values of q, say larger than 1.0 a.u., the agreement is
satisfactory, but for small values the discrepancy is obvious. With the MSC model the disagreement is about half the signal. Even with the MO calculation the difference is 1.5% of $J(0)$. This tends to confirm that the main effect which decreases the difference with experiment is the consideration of H-H interactions; it is not taken into account in the MSC model, although its molecular wave function can be considered to have a better basis set than the MO-LCAO calculation. The same discrepancy with experiment has been found for the $<110>$ direction.

Figure 2 shows the anisotropy of the Compton profiles, i.e. the difference between $<100>$ and $<110>$ DCP's. The disagreement is total with MSC, as expected from previously, but the agreement with MO is surprisingly good from $q=0.5$ a.u. For low $q$, corresponding in $r$ space to fairly large distances, the disagreement can be due to the preponderant part of the medium range interaction between high order neighbours or to the absence of consideration of hybridization with unoccupied orbitals, because one can admit that the crystal symmetry is properly treated in this model.

2. LITHIUM GRAPHITE INTERCALATION COMPOUND.

Two measurements have been performed on LiC$_6$, with the scattering vector respectively parallel and perpendicular to the $c$ axis of the compound. As the layered structure of graphite is basically conserved in the graphite intercalation compound LiC$_6$, the simplest model -the rigid band model- neglects any hybridization between lithium and graphite orbitals. This model considers that the band structure is at first order the graphite one, modified on two points. As the unit cell of LiC$_6$ is larger, the band structure of graphite is folded into the Brillouin zone of LiC$_6$, and the Fermi level is raised to accommodate the lithium 2s extra electron. More sophisticated models have been proposed. The last one to date (5) is a self consistent pseudopotential calculation using the local density functional approximation. The pseudo wave function is developed on a mixed basis consisting of 2s and 2p atomic orbitals both on lithium and carbon sites for the localized orbitals, and of plane waves for extended orbitals.

To evidence the effect of the intercalation of lithium on the electron momentum density (EMD), a difference profile is performed from the graphite profile subtracted from the LiC$_6$ profile (5). This can be separated in two contributions: the valence band and the conduction band. The modification of the EMD in the valence band, filled $\sigma$ and $\pi$, is due to the lithium which delocalizes these electrons towards interlayer space. So there is a distortion of these bands compared to the graphite ones. The conduction profile difference has been calculated (5) and it is shown on figure 3 for the scattering vector parallel to the $c$ axis; this difference profile is indeed only the LiC$_6$ $\pi^*$ Compton profile because graphite is a semi metal with an overlap of 0.01 eV between $\pi$ and $\pi^*$, so the conduction band is admitted to be empty, at the precision of the calculation. This profile is modulated by the shortest reciprocal lattice vector parallel to $c$, indicating a succession of occupied and unoccupied states. As the conduction profile
has no contribution for \( q = 0.0 \), because of the antisymmetric nature of the wave function, it means that it is almost not hybridized with lithium states, because any lithium electron profile would have non zero value for \( q = 0 \). This means that the interaction between lithium and conduction band is much weaker than for valence band, and especially the \( \pi \) orbitals as they are located in the interlayer region in pure graphite.

The modification of the density caused by the lithium is actually represented by the sum of the valence and conduction profile differences as we defined them previously. It is presented on figure 4, both experimental and computed. The nice agreement between experiment and the recent calculations shows the quality of the basis set used in this model. The profile difference, corresponding to the initial \( 2s \) lithium electron, has a component at zero, indicating the hybridization occurring preferentially with valence bands, so it shows the failure of the rigid band model. Moreover, this difference profile is particularly localized in momentum space, i.e. delocalized in position space, because of the hybridization of the \( \pi \) orbital originating from graphite with the lithium orbitals, leading to the metallic character of the intercalated compound.

REFERENCES
1 Aikala O., Jokela V., Mansikka K., J. Phys. C6 (1973) 1116; Aikala O., Phil. Mag. 21 (1975) 935.