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Theoretical Compton profile anisotropies in solid lithium hydride

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The Compton profiles of LiH crystal are computed for several directions of the scattering vector within the tight-binding formalism. Starting from the first-order density matrix of the crystal, a compact analytic expression of the directional Compton profiles is provided. The results are compared with experimental data and with previous calculations.

I. INTRODUCTION

Solid lithium hydride, which is the simplest heteronuclear crystal, has received considerable attention, not only for its intrinsic interest but also as a test before considering more complicated systems. From the point of view of the comprehension of the electronic properties, one of the major difficulties of LiH is constituted by the very diffuse nature of the hydride-ion wave functions. This circumstance explains the large experimental and theoretical interest of physicists in Compton scattering in LiH, following the pioneering experiments of Phillips and Weiss.[1] In fact it is well known that Compton profiles at small momentum provide a sensitive tool for investigating the outer-shell-electron wave functions (for a review of theoretical and experimental aspects see, for instance, papers[2,3] and reference quoted therein).

Measurements of Compton profiles in LiH were performed by Felsteiner *et al.*[4] and Paakkari *et al.*[5] on polycrystalline samples: their results can therefore be compared with the spherically averaged theoretical calculations. Isotropic Compton profiles in LiH have been computed by several authors with different functions. Brandt[6] used an electronic wave function in the cell approximation. Berggren and Martino[7] performed a calculation within the linear combination of atomic orbitals (LCAO) formalism. These authors[7] first showed that a correct account of overlap effects is essential to bring the theoretical results into agreement with experiments. Felsteiner *et al.*[4] in their calculations used numerical self-consistent local orbitals. Refined procedures for constructing the crystal density matrix have been provided by Paakkari *et al.*[5] with the method of linear equations and by Grosso *et al.*[8,9] with group-theory techniques. These authors [5,8] showed that excellent agreement with experiment could be achieved adopting the ionic picture of LiH, with Hurst's[10] wave functions for hydride ions, and including overlap effects up to a large number of neighbors.

Recently accurate experimental measurements of the directional Compton profiles in LiH have been performed by Reed[11] for several orientations of the scattering vector; the directional profiles previously reported in the literature[1] concerned a smaller number of crystal orientations with less statistical accuracy.

The first calculation of anisotropic effects in LiH Compton profiles was performed by Berggren.[12] Aikala[13] followed a similar LCAO procedure but with a more complete treatment of the overlap effects. Then Ramirez *et al.*[14] extended to LiH the molecular simulated crystal (MSC) procedure applied to the lithium fluoride crystal.

In Sec. II, we present a calculation of directional Compton profiles in LiH within the tight-binding approximation. The first-order density matrix of the crystal is expressed in terms of localized Slater-type orbitals (STO), which are then expanded into Gaussian-type orbitals (GTO). The novelty of our procedure is that a simple and compact analytic expression for the directional Compton profiles is provided. In Sec. III, our results are compared with experimental data and with previous calculations. Section IV contains the conclusions.

II. EXPRESSION OF DIRECTIONAL COMPTON PROFILES IN LiH CRYSTAL

The crystal structure of LiH is fcc with lattice constant $a = 7.72$ a.u. The hydride and lithium ions in the unit cell are in the positions $\vec{d}_1 = 0$ and $\vec{d}_2 = (a/2)(1,0,0)$. In the ionic picture Li^+ and H^- ions have the simple $1s^2$ closed-shell electronic configuration. The $1s$ functions are taken in the form $\phi(\vec{r}) = (\zeta^3/\pi)^{1/2} e^{-\zeta r}$, with optimized screening $\zeta_{Li} = 2.6875$ (free-ion approximation) and $\zeta_H = 0.772h$ (hydride ion[10] in the point-charge field of the rest of the lattice).

The computation of Compton profiles requires the explicit knowledge of the first-order density matrix.[15] For the closed-shell LiH system, the spinless density matrix can be written as

$$\rho(\vec{r},\vec{r}\,')=2\sum_{\mu\nu}\sum_{\vec{\tau}_m\vec{\tau}_n}\phi_\mu^*(\vec{r}-\vec{d}_\mu-\vec{\tau}_m)\times T_{\mu\vec{\tau}_m,\nu\vec{\tau}_n}\phi_\nu(\vec{r}\,'-\vec{d}_\nu-\vec{\tau}_n)\,, \quad (1)$$

where $\vec{\tau}_m, \vec{\tau}_n$ are translation vectors, μ and ν label either hydride or lithium ions, and T is the inverse of the overlap matrix. An elegant method for the evaluation of the matrix T in closed-shell crystals has been given in previous papers.[8,9] In the particular case of LiH, such a method has provided a quite good account of the isotropic Compton profile,[8] x-ray structure factors,[9] and diamagnetic susceptibility.[16]

The electron momentum density is

$$\rho(\vec{p})=\frac{1}{(2\pi)^3}\int\int\rho(\vec{r},\vec{r}\,')e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')}d\vec{r}\,d\vec{r}\,'. \quad (2)$$

Within the impulse approximation, the Compton profile for a given direction of the scattering vector (referred to as z direction) is

$$J(p_z)=\int\int\rho(\vec{p})dp_x dp_y\,. \quad (3)$$

If the wave functions in Eq. (1) are left in the form of 1s STO's, the maximum of simplification which can be achieved in Eq. (3) is its reduction to a series of one-dimensional integrals to be evaluated numerically for each p_z and for each direction.[13] In the present paper we have found it convenient to express the STO's in Eq. (1) in terms of GTO's; in this way we have been able to obtain a compact analytic expression for the directional Compton profiles. For a review on techniques and applications of the Gaussian representation[17] of atomic-like orbitals, we refer to the paper of Brener and Fry.[18] The Gaussian representation has been recently adopted in the calculation of the Hartree-Fock energy bands[19] of lithium hydride.

We thus expand 1s STO's into a finite number of 1s GTO's. Using the scaling theorem,[20] we write

$$\phi_{1s}(\vec{r})\equiv\left(\frac{\zeta^3}{\pi}\right)^{1/2}e^{-\zeta r}\cong\sum_{i=1}^{N}c_i\left(\frac{2\alpha_i\zeta^2}{\pi}\right)^{3/4}e^{-\alpha_i\zeta^2 r^2}\,. \quad (4)$$

The 5G representation of 1s STO's has been chosen after checking its practical equivalence from a numerical point of view. For $N=5$ we have used the optimized parameters α_i and c_i given in Ref. (21). These are $\alpha_1=7.445\,27\times10^{-2}$, $\alpha_2=1.975\,72\times10^{-1}$, $\alpha_3=5.786\,48\times10^{-1}$, $\alpha_4=2.071\,73$, $\alpha_5=1.130\,56\times10^{1}$, $c_1=1.935\,72\times10^{-2}$, $c_2=4.825\,70\times10^{-1}$, $c_3=3.318\,16\times10^{-1}$, $c_4=1.135\,41\times10^{-1}$, and $c_5=2.214\,06\times10^{-2}$.

We now put Eq. (4) into Eq. (1) and Eq. (1) into Eq. (2) remembering that the Fourier transform of a Gaussian function is still a Gaussian function. We then perform a coordinate transformation in such a way as to line up the scattering vector with the p_z axis and finally perform the integration (3). With somewhat laborious but straightforward calculations we obtain for the directional Compton profiles at momentum q and scattering vector $\vec{s}$:

$$J_{\vec{s}}(q)=J_{\vec{s}}^{\mathrm{Li}}(q)+J_{\vec{s}}^{H}(q)\,, \quad (5)$$

where

$$J_{\vec{s}}^{\mathrm{Li}}(q)=4\sqrt{\frac{2}{\pi}}\sum_{\vec{R}_m}\sum_{ij}^{N}c_ic_j\,T_{\mathrm{Li}m}\frac{a_{\mathrm{Li}m}^{1/4}}{(\alpha_i\zeta_{\mathrm{Li}}+\alpha_j\zeta_m)^2}\times e^{-a_{\mathrm{Li}m}(\vec{s}\times\vec{R}_m)^2}e^{-q^2/ha_{\mathrm{Li}m}}\times\cos(\vec{s}\cdot\vec{R}_m q)$$

A similar expression holds for $J_{\vec{s}}^{\mathrm{H}}(q)$. In Eq. (6) the sum over $\vec{R}_m$ extends over the 179 ions contained in the first 12 shells. The elements of matrix T are given in Ref. (9) and $a_{\mathrm{Li}m}$ is defined as

$$a_{\mathrm{Li}m}=\frac{\alpha_i\zeta_{\mathrm{Li}}^2\alpha_j\zeta_m^2}{\alpha_i\zeta_{\mathrm{Li}}^2+\alpha_j\zeta_m^2}\,.$$

The profiles (5) are normalized to 4 electrons; atomic units are used throughout this work.

TABLE I. Theoretical directional Compton profiles for LiH. Atomic units are used.

			$J(q)$		
q	⟨100⟩	⟨110⟩	⟨111⟩	⟨112⟩	⟨221⟩
0.0	2.256	2.189	2.273	2.264	2.241
0.1	2.222	2.169	2.242	2.226	2.212
0.2	2.111	2.113	2.144	2.124	2.128
0.3	1.956	2.014	1.979	1.977	1.993
0.4	1.756	1.849	1.773	1.792	1.806
0.5	1.539	1.610	1.545	1.567	1.573
0.6	1.316	1.331	1.305	1.316	1.315
0.7	1.101	1.064	1.069	1.071	1.067
0.8	0.906	0.847	0.864	0.861	0.858
0.9	0.741	0.688	0.706	0.701	0.698
1.0	0.611	0.576	0.591	0.587	0.583
1.1	0.512	0.498	0.506	0.504	0.501
1.2	0.438	0.438	0.440	0.441	0.439
1.3	0.381	0.390	0.387	0.390	0.390
1.4	0.336	0.349	0.344	0.346	0.347
1.5	0.299	0.312	0.308	0.309	0.310
1.6	0.267	0.278	0.277	0.276	0.277
1.7	0.240	0.248	0.249	0.247	0.248
1.8	0.216	0.221	0.223	0.221	0.222
1.9	0.195	0.198	0.200	0.198	0.199
2.0	0.176	0.177	0.178	0.177	0.177

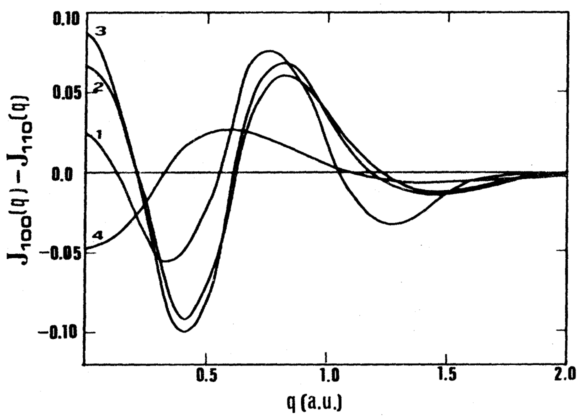

FIG. 1. Theoretical and experimental Compton profile anisotropies $J_{100}(q)-J_{110}(q)$ in LiH crystal. Curve 1 gives the experimental results of Reed (Ref. 11). Curves 2, 3, and 4 are the theoretical results of the present work, Aikala (Ref. 13), and Ramirez *et al.* (Ref. 14), respectively.

III. RESULTS AND DISCUSSION

The Compton profiles of LiH obtained from Eq. (5) with the scattering vector in the directions ⟨100⟩, ⟨110⟩, ⟨111⟩, ⟨112⟩, and ⟨221⟩ are reported in Table I. These directions have been chosen because of the availability of experimental data[11] and other theoretical calculations. In Fig. 1 we report, as an example, the Compton profile anisotropies $J_{100}(q)-J_{110}(q)$. For comparison the theoretical anisotropies of Aikala[13] and Ramirez *et al.*[14] and the experimental results of Reed,[11] corrected for spectrometer resolution and multiple-scattering effects, are also given.

In order to condense in a single parameter the discrepancies between theory and experiment, we define the ratio

$$R=\frac{\int |J_{\mathrm{meas}}(q)-J_{\mathrm{calc}}(q)|\,dq}{\int J_{\mathrm{meas}}(q)dq}\,, \tag{7}$$

where $J_{\mathrm{meas}}(q)$ are the experimental data of Reed[11] (normalized to 4). The values of R for several directions of the scattering vectors are reported in Table II. From this table it can be safely inferred that the ionic picture for LiH is in much better agreement with experiment than the molecular simulated crystal procedure. Table II also shows the excellent agreement between our results and the experimental values.[11] This fact is likely to be due to the accurate procedure adopted in constructing the crystal density matrix and to the simplifications introduced by the Gaussian representation of Slater-type orbitals.

TABLE II. Values of the parameter R, defined by Eq. (7) for several directions of the scattering vector.

	This work	Aikala (Ref. 13)	Ramirez *et al.* (Ref. 14)
R_{100}	0.0227	0.0313	0.1735
R_{110}	0.0093	0.0271	0.1756
R_{111}	0.0147	0.0246	0.1705
R_{112}	0.0133		
R_{221}	0.0087		

A rather subtle point concerns the behavior of $J_{\vec{s}}(0)$ as a function of the direction of the scattering vector. The theoretical calculations (Table I) give the sequence $J_{110}(0)<J_{221}(0)<J_{100}(0)<J_{211}(0)<J_{111}(0)$. The experimental data[11] confirm our theoretical sequence except for $J_{221}(0)$ [the disagreement for ⟨221⟩ direction, which is experimentally the most difficult of the five directions to identify, is still to be clarified]. However, the experimental anisotropy $J_{110}(0)-J_{100}(0)=-0.025$ is smaller than the theoretical anisotropy −0.067. As noted in the literature,[14] a partially covalent-type bonding should decrease this difference and could bring the experimental and theoretical anisotropies in closer agreement. From these considerations, and from the band structure[19] of LiH, it can be inferred that the ionic picture of LiH should be refined by allowing some mixing of 2*s* functions of lithium.

IV. CONCLUSIONS

In this paper we have calculated directional Compton profiles of lithium hydride. A numerically simple procedure is obtained using the Gaussian representation of atomiclike orbitals. The results are in better agreement with experimental measurements than previous calculations. The method employed can be easily extended, by a differentiation technique, to more complicated situations involving 2*s*, 2*p*, etc. atomic orbitals.

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