

Anisotropic Compton Scattering in LiF

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Both experimental measurement and theoretical calculations of the Compton profiles of LiF indicate a significant anisotropy in the electron momentum distribution whereas published x-ray structure-factor data indicate a lack of anisotropy in the charge density. In this paper we show that momentum distributions can be orders of magnitude more sensitive to anisotropy in the electron distributions than x-ray structure factors, at least in materials where the overlap of the wave functions is small.

Since its resurgence in the late 1960's, Compton scattering has promised to be a delicate probe of the electronic structure of atoms, molecules, and solids.^{1,2} Our understanding of this technique has matured to the extent that we may now test its performance in comparison with more traditional methods such as elastic x-ray scattering and theoretical calculations for simple solid-state systems. In this Letter we choose to consider the anisotropy of the Compton scattering in LiF for the following reasons: (a) There have been extensive experimental studies of the x-ray form factors over a long period of time³⁻⁶; (b) the electronic structure of LiF is simple so that highly accurate wave functions are readily available; and (c) the results of recent Hartree-Fock calculations⁷ on LiF differ from both our measured and calculated anisotropies.

The question of the size of the anisotropy of the charge density in LiF has been studied by elastic x-ray scattering.³⁻⁶ The most recent conclusion drawn from an analysis of these measurements is that the charge density, to within the experimental accuracy, is isotropic, i.e., the charge is spherically symmetrical about each ion.⁶ Since Compton scattering, unlike elastic x-ray scattering, is related to both the off-diagonal and diagonal elements of the density matrix, one would expect it to yield more complete information about these anisotropies. Both our experimental and theoretical results indicate that this is indeed the case.

The formal definitions for the Compton profile

and form factor for a one-electron wave function $\Psi(\vec{r})$ and the momentum transfer \vec{k} are given by

$$J(q) = \int N(\vec{p}) dp_\alpha dp_\beta, \quad (1)$$

$$F(\vec{k}) = \int e^{-i\vec{k}\cdot\vec{r}} |\Psi(\vec{r})|^2 d^3r, \quad (2)$$

where $q = (\vec{k}\cdot\vec{p})/k$, $p_\alpha \cdot \hat{k} = 0$, and

$$N(\vec{p}) = \chi(\vec{p})\chi^*(\vec{p})$$

with $\chi(\vec{p})$ the Fourier transform of the spatial wave function

$$\chi(\vec{p}) = (2\pi)^{-1/2} \int \Psi(\vec{r}) e^{i\vec{p}\cdot\vec{r}} d^3r. \quad (3)$$

For the case of periodic systems, such as LiF, one has of course that \vec{k} in $F(\vec{k})$ is limited to reciprocal-lattice vectors whereas there is no such restriction for the Compton profile. The anisotropy of the Compton profile is measured by fixing $|\vec{k}|$ but varying its orientation with respect to the crystal symmetry axes.² The anisotropy is defined as the difference between the profiles for different directions, i.e., $\Delta J = J_1(q) - J_2(q)$.

The γ -ray Compton measurements were performed in the manner described in Ref. 2. The data for the profile anisotropy was collected on a single-crystal cylinder of LiF, 1.27 cm in diameter and 2.54 cm long with a $\langle 110 \rangle$ axis parallel to the cylinder. Data were collected for the scattering vector parallel to $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ axes with $\sim 1.7 \times 10^5$ counts collected in the peaks. The profiles were normalized to six electrons for $0 \leq q \leq 15$ a.u.

The effect of multiple scattering is, to first or-

der, only to decrease the amplitude of the measured anisotropy and not alter its shape.^{8,9} Any photon scattered more than once is expected to lose its orientational information. The percent of photons multiply scattered can be estimated from both a simple calculation which ignores photoelectric losses and an analysis of data taken on samples as a function of thickness. The calculation gives an amplitude enhancement factor for the measured anisotropy of 1.27 whereas the analysis of the experimental data gives a factor of 1.28. Since our experimental accuracy for the anisotropy is $\pm 12\%$, a 1% uncertainty in the multiple-scattering correction is well within our stated error. The corrected experimental anisotropies are shown as solid lines in Fig. 1. The data have not been corrected for instrumental resolution but instead the theoretical profiles have been convolved with the resolution function for comparison.

The primary reason for the simplicity of the theoretical description of the LiF crystal is the small overlap between closed-shell ions. To a good approximation the total wave function can be written as a superposition of the free-ion solutions. A number of calculations of total energy, lattice constant,¹⁰ form factors,^{11,12} and spherically averaged Compton profiles¹³⁻¹⁵ have achieved substantial agreement with experiment with such a description. This success indicates that electron correlation is relatively unimportant for an accurate description of the ground-state properties of LiF. Indeed one might in many respects regard LiF as being the "hydrogen atom" of solid-state physics.

Our calculations of the anisotropic profiles are based on a total wave function which is a superposition of ionic solutions. To test the presumption that effects of relaxation of the orbitals due to the crystalline environment are small we have used both the free- and relaxed-ion orbitals of Kunz.¹⁶ The anisotropy of the profiles calculated from the relaxed orbitals are shown in Fig. 1. Differences due to relaxation were virtually negligible. The agreement with experiment is within experimental error which is particularly satisfying since the anisotropy represents only a few percent of the total Compton profile.

The results of Euwema *et al.*⁷ are also shown in Fig. 1. The agreement of these calculations are considerably poorer than for our own results. The disagreement, particularly in the small-momentum region, may be due to the use of a Gaussian basis set by Euwema *et al.* The small-

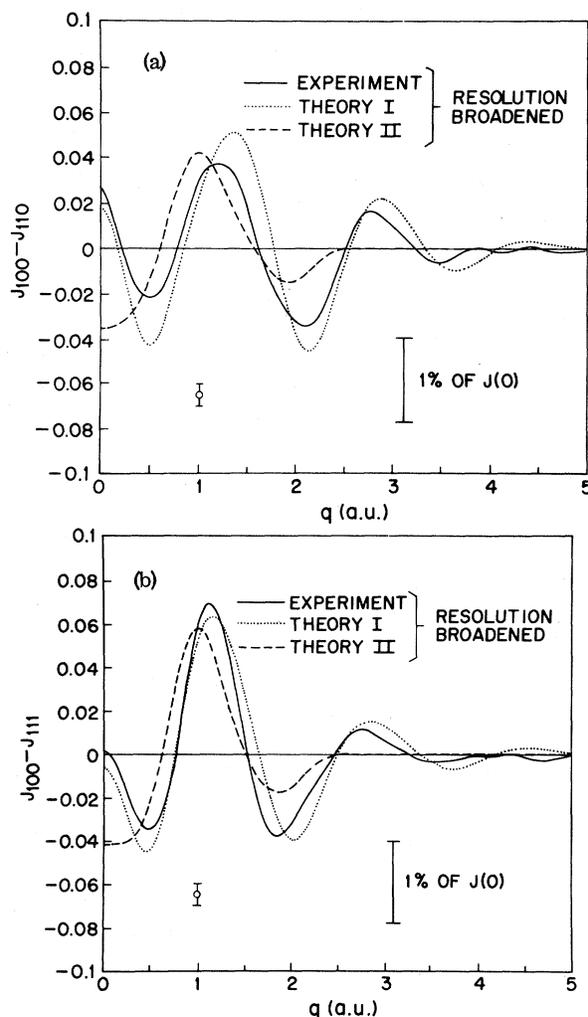


FIG. 1. Anisotropy of the Compton profiles of LiF: (a) $J_{100} - J_{110}$, (b) $J_{100} - J_{111}$. Theory I from our calculations, Theory II from Ref. 7. The effect of the spectrometer's finite resolution has not been removed from the experimental data but instead the theoretical profiles were convolved with the resolution function which is a Gaussian with $\sigma = 0.202$.

momentum region corresponds to the tail region of the orbitals, which is most difficult to represent accurately by Gaussians.

We now return to the problem of elastic x-ray scattering factors and pose the question of why these experiments, which claim an accuracy of the same order of magnitude as our own, are apparently not as sensitive to anisotropies.

The reason lies in the above mentioned dependency of the elastic scattering factors on only the diagonal elements of the density matrix. This results in a "smearing out" of anisotropies, as compared with Compton scattering. For any

form of anisotropic charge density the anisotropy in the Compton profile is orders of magnitude larger than that for the form factor for smaller values of q , and the smaller the magnitude of the anisotropy, the larger the q values at which the most significant part of the form-factor anisotropy occurs. In the case where the anisotropy results from overlapping charges, the anisotropy of the Compton profile goes linearly with the overlap, whereas the form-factor anisotropy goes effectively worse than the square of the overlap.^{17,18} Furthermore there is a coherent constructive enhancement in certain directions of momentum space which increases the Compton anisotropy, and in most cases no such enhancement occurs in elastic scattering. These effects are simply illustrated in the case of an ionic crystal with small overlap, where we may expand the wave functions in the overlap. Then the leading anisotropic part of the form factor due to an orbital of type ν at site \vec{R}_g overlapping an orbital of type μ at site $\vec{R}_{g'}$, at wave vector \vec{k} , is given by

$$2S_{\nu\mu} \int \psi_\nu^*(\vec{r} - \vec{R}_g) \psi_\mu(\vec{r} - \vec{R}_{g'}) e^{i\vec{k}\cdot\vec{r}} d^3r, \quad (4)$$

where the overlap is given by

$$S_{\nu\mu} = \int \psi_\nu(\vec{r} - \vec{R}_g) \psi_\mu(\vec{r} - \vec{R}_{g'}) d^3r. \quad (5)$$

The anisotropic part clearly goes as overlap times the Fourier transform of overlap which is thus less than the overlap squared. The equivalent term for the Compton profile is given by

$$2S_{\nu\mu} \int \chi_\nu^*(\vec{p}) \chi_\mu(\vec{p}) \exp[i\vec{p}\cdot(\vec{R}_g - \vec{R}_{g'})] d\vec{p}_x d\vec{p}_y. \quad (6)$$

The Fourier transforms are given by Eq. (3) and clearly are not site dependent and thus do not overlap in p space. The constructive enhancement mentioned above comes from the expression $\exp[i\vec{p}\cdot(\vec{R}_g - \vec{R}_{g'})]$ in the Compton profile which has become known as the diffraction effect.¹⁹ Calculations of LiF show that $\Delta F/F(0)$ is orders of magnitude smaller than in $\Delta J/J(0)$ over the range of q or k for which either $J(q)$ or $F(k)$ is larger than a few percent of its maximum. For example, we find that the anisotropy of the form factors¹² $[F(511) - F(333)]/F(0) \approx 1 \times 10^{-5}$ and $[F(711) - F(551)]/F(0) < 10^{-5}$ which approximate the anisotropies $[100] - [111]$ and $[100] - [110]$, respectively. From Fig. 1 one sees that $\Delta J/J(0)$ is of the order 10^{-2} to 10^{-3} . Typical values for nearest-neighbor overlap $S_{\nu\mu}$ in LiF are 10^{-2} and thus the fact that form-factor anisotropies depend upon $S_{\nu\mu}^2$ while Compton-profile anisotropies vary only as $S_{\nu\mu}$ explains the 10^2 larg-

er anisotropy in the Compton profile. We conclude that to measure the anisotropy in the charge distribution in LiF by elastic x-ray scattering, the experiments would have to be orders of magnitude more accurate.

Yet there are factors which make it very difficult to obtain in elastic scattering an accuracy even as good as that obtainable by Compton scattering. Among these are large corrections for systematic effects such as extinction. In addition one can only measure the form factor at discrete values of k . Thus both the physics and the nature of the experiments dictate the use of the Compton-scattering technique to measure anisotropies in electron distributions.

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wave functions, the Compton-profile anisotropy would be independent of overlap while the form factor would have a linear dependence on the Fourier transform of the overlap term. Thus the ratio of the anisotropic term

in the form factor to that in the Compton profile would be the same as in our linear combination of atomic orbitals approach.

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Evidence for a Surface-State Exciton on GaAs(110)*

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Synchrotron-radiation photoemission data are obtained from GaAs($\bar{1}\bar{1}0$) and (110) faces for *s* and *p* polarization which show an enhancement of valence-electron emission for initial states at and below the valence-band maximum when the photon energy is scanned through the threshold for Ga-3*d*-core to intrinsic-surface-state excitations. The enhancement is interpreted as a core surface exciton associated with the Ga dangling bonds.

The use of photoemission spectroscopy to investigate properties of occupied surface states has been extended recently to the study of empty surface states. Eastman and Freeouf have reported such unoccupied states just below the bottom of the conduction-band minimum in both Ge and GaAs.^{1,2} We have performed more extensive photoemission measurements on Zn-doped *p*-type GaAs which indicate that the excitations observed by Eastman and Freeouf are not surface states in the conventional sense, but are more properly thought of as "surface excitons." We believe that these results represent the first identification of surface excitons.

The photoemission techniques used here exploit both the continuum nature and strong polarization of the synchrotron radiation from the storage ring at the University of Wisconsin Physical Sciences Laboratory.³ Rather than measure the energy distribution curve (EDC) of photoemitted electrons we measure what we call the constant initial-energy spectrum (CIS). This is done by monitoring the electron counting rate as the photon energy $h\nu$ and kinetic-energy window E_f of our analyzer are swept synchronously so that $h\nu - E_f = -E_i$ remains constant, where E_i is the initial-state energy. An alternate mode of operation which we refer to as the constant final-energy spectrum (CFS) is obtained by sweeping $h\nu$ while keeping E_f constant. The "partial-yield" curves reported in Ref. 1 are CFS's in our terminology.² Descriptions of the CIS and CFS modes have been reported elsewhere.^{4,5} To probe the properties of the empty surface states, one has to detect the photoemissive contribution

which results from core to surface-state excitations through the intermediary of a decay process.^{1,4} As discussed below, measurement of CIS's rather than CFS's permits one to distinguish between two alternative decay processes for photoexcited electrons. Further, CIS data are obtained for each of the four cases where the polarization \hat{E} is perpendicular or nearly parallel to the Ga dangling bond or the As dangling bond.

The transitions at issue in these experimental studies are those that occur at the threshold for excitation of the Ga-3*d*-core states lying 18.7 ($d_{5/2}$) and 19.2 ($d_{3/2}$) eV below the valence-band maximum, which is chosen for the energy zero. The latter binding energies are obtained from EDC and CFS data and are consistent with those in the literature.¹ The narrow pair of peaks found near 20 eV in the CIS's of Fig. 1 are attributed to an enhanced emission level occurring at the core threshold. The doublets are split by the core-spin-orbit splitting.¹ The structures occurring at lower energies are due to valence-electron excitations and are shown for the purpose of establishing a reference level for the strength of the enhancement doublets. The term valence electron is used instead of valence band because valence surface states probably contribute to the emission⁶; however, their properties do not directly bear on the issue. Each spectrum in Fig. 1 is obtained for different polarization and/or crystal orientations but the same $E_i = -1.2$ eV; E_i is a parameter for CIS's. For the upper curve in Fig. 1—($\bar{1}\bar{1}0$) face and *p* polarization—the doublet occurs at 19.65 and 20.15 eV