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Compton Profile of LiH

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The Compton profile from a single crystal of LiH has been measured with the x-ray scattering vector along the [100], [110], and [210] directions. The valence-electron contribution to the measured profile is in marked disagreement with that calculated from the crystal-field wave functions of Hurst. The observations indicate that the valence-electron momentum distribution is broader in momentum space than the distribution obtained from a superposition of H^- and Li^+ wave functions for either the free ions or the H^- ion in a Li^+ point-lattice crystalline field. It appears that a more extensive calculation is required to get agreement with both the x-ray scattering factor and Compton-profile measurements. For the three crystal orientations studied, the Compton profiles show only a small anisotropy.

INTRODUCTION

IT is known that LiH crystallizes in the rock-salt structure. It is one of the simplest crystalline materials in the sense that there are only four electrons per molecule, and two electrons are in the 1*s*-like core of the Li ion. Calder *et al.*[1] have measured the LiH x-ray scattering factors, and Hurst[2] has evaluated the scattering factors from wave functions determined by minimizing the energy of the H^- ion in the point-lattice crystalline field of the Li^+ ions. The Hurst calculation gives scattering factors in good agreement with the measurements. With the recent development of high-resolution Compton-profile measurements,[3] we have been able to compare the experimentally determined electron momentum densities with those deduced from both the Hurst and the free-ion wave functions. The agreement is poor, pointing out the sensitivity of the Compton profile to the valence-electron wave functions.

EXPERIMENT

A clear LiH single crystal approximately cubic in shape (0.7 cm on a side) was used with the Compton-scattering apparatus previously described.[3] A Mo-target spectrographic x-ray tube, LiF crystal analyzer [(400) Bragg reflection], and Compton scattering angle $2\theta_c$ of $(117\pm1)°$ were employed. The total instrumental width due to divergences of the analyzing-system slits, the mosaic spread of the LiF crystal, and the finite range of $2\theta_c$ was 0.28 a.u. (full width at half-maximum in atomic units of momentum). By rotating the LiH crystal about a [100] axis, the sample was oriented with the x-ray scattering vector approximately along the [100], [110], and [210] directions, respectively. The orientations were established by observing Bragg scattering of continuum radiation from the sample. Several runs were made for each orientation so that approximately 50 000 x rays were counted per datum point in the center region of the Compton profile at analyzing crystal 2θ intervals of 0.02° (0.037 a.u. of momentum). The ratio of Mo$K\alpha$ intensity to the background continuum intensity at the center of the Compton peak was 9.9/1.

RESULTS

In order to obtain the experimental Compton profiles $J(z)$ (z is the electron-momentum component along the scattering vector), the data (x-ray intensity versus analyzing-crystal angle 2θ) were analyzed in the following way. A correction linear in wavelength was applied to the data to approximately account for the wavelength dependence of sample absorption and analyzer reflectivity, and electron recoil. The Rachinger[4] method was then used to separate the $K\alpha_1$ component from the corrected intensity, after the background due to Compton scattering from the bremsstrahlung continuum and cosmic rays had been subtracted. Instrumental broadening (a small effect in the LiH profiles) was essentially removed by an iterative procedure in which successive trial profiles were convolved with the known instrumental-resolution function until agreement with the $K\alpha_1$ component was obtained. The correct trial profile was then folded about its centroid (for $-1.5\text{ a.u.}<z<1.5\text{ a.u.}$) and the resultant curve averaged. (Because of 1*s*-core binding effects, only data from the long-wavelength side of the profile were used for $|z|>1.5$ a.u.). This curve (half of the total profile), averaged over the three crystal orientations studied and normalized to have an area of two electrons (half of the total number of electrons), is shown in Fig. 1 [$J(z)$]. Also shown are $J(z)$ curves for a superposition of H^-

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[2] R. P. Hurst, Phys. Rev. **114**, 746 (1959).

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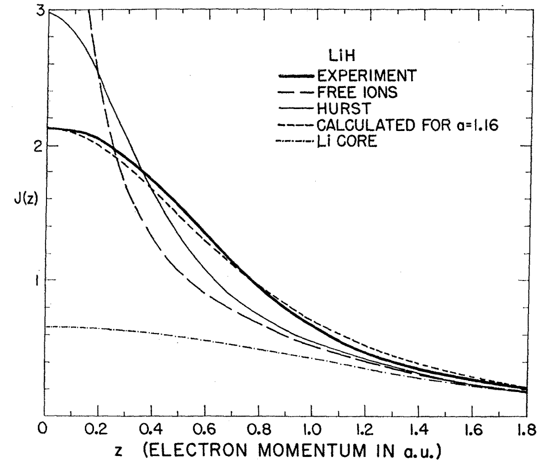

FIG. 1. Compton profiles for LiH (four electrons per molecule). The experimental curve is the average of $J(z)$ for the three crystal orientations studied. For each orientation, the measured $K\alpha_1$ component (with background subtracted, corrected for the wavelength dependence of sample absorption, analyzer reflectivity, and electron recoil, and with instrumental broadening removed) was folded about $z=0$ (for -1.5 a.u.$<z<1.5$ a.u.), and the resultant curves averaged. The calculated curves are for (a) a superposition of H^- and Li^+ free ions (Ref. 5); (b) a superposition of H^- and Li^+ ions for Hurst's open configuration (Ref. 2); (c) a superposition of H^- and Li^+ ions for Hurst's closed configuration with $\alpha=0$ and $a=1.16$; and (d) the Li^+ free-atom $1s^2$ core (Ref. 6).

and Li^+ free ions,[5] for a superposition of H^- and Li^+ ions calculated from (a) Hurst's open-configuration crystalline-field wave functions[2] and (b) Hurst's closed configuration with the orbital exponent adjusted to give a best fit to the measured $J(z)$, and for the free-atom $1s^2$ Li^+ core.[6] It is evident that none of these calculations is in agreement with the experimental results. The free-ion calculation shows the largest discrepancy with experiment, a factor of 2 at $J(0)$, and the energetically unfavorable closed-configuration calculation with $a=1.16$ gives the best fit (see the discussion below).

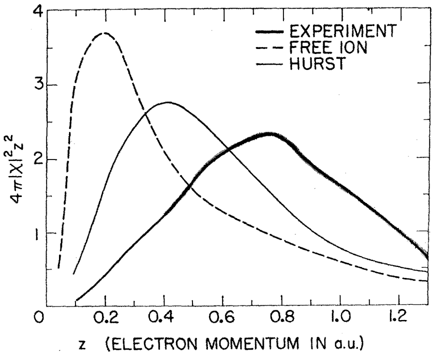

FIG. 2. Valence-electron radial momentum distributions $4\pi|\chi|^2z^2$ for LiH (two electrons per molecule), obtained from the corresponding $J(z)$ curves shown in Fig. 1 with the free-atom Li^+ $1s^2$ core subtracted. The shading indicates the uncertainty in determining the slope of the experimental $J(z)$ curve.

The valence-electron $J(z)$ curves for the three crystal orientations were obtained by subtracting from each measured $J(z)$ curve the calculated free atom $1s^2$ $J(z)$ with an area equal to half the area of the measured curve. The results are summarized in Table I.

The electron momentum component z along the scattering vector is related to the parameter q commonly used to convert from a wavelength to a momentum scale by the following expression:

$$q(\lambda)\equiv\frac{mc}{2\lambda_0\sin\theta_c}\left[\lambda-\left(\lambda_0+\frac{2h}{mc}\sin\theta_c\right)\right],$$
$$z=q\left[1+\frac{\lambda-\lambda_0}{\lambda_0}+\left(\frac{\lambda-\lambda_0}{2\lambda_0\sin\theta_c}\right)^2\right]^{-1/2}, \tag{1}$$

where λ_0 is the wavelength of the incident x ray ($\lambda_0=0.70930$ Å for Mo$K\alpha_1$), $mc=137.04$ a.u., and $2h/mc=0.048524$ Å.

For polycrystalline samples the Compton measurement averages over all directions in momentum space. Thus $J(z)$ and the momentum density $4\pi|\chi(p)|^2$ are related by the expression[3]

$$J(z)=2\pi\int_{|z|}^{\infty}|\chi(p)|^2p\,dp, \tag{2}$$

and the radial momentum distribution $4\pi p^2|\chi(p)|^2$ (radial in momentum space, not configuration space) can be obtained from the slope of $J(z)$;

$$4\pi|\chi|^2p^2=2|z\,dJ/dz|. \tag{3}$$

Because the measured anisotropy in $J(z)$ is small for the three crystal orientations studied, an approximate valence-electron radial momentum distribution could be obtained from Eq. (3) from the average of the three valence-electron $J(z)$ curves. The resulting distribution is shown in Fig. 2, together with the radial momentum distribution of the valence electrons calculated from the Hurst wave functions and from the free-ion wave functions. The experimental results show a momentum distribution significantly broader than these calculations, whereas the x-ray scattering factors calculated from the Hurst wave functions are in reasonable agreement with the measured scattering factors (see Table I). The angular correlation of photons from positron annihilation in LiH has been measured by Stewart and March.[7] The measured annihilation-curve half-width [about 15% less than the measured $J(z)$ half-width] also suggests a valence-electron momentum distribution considerably broader than the above calculations, although the interpretation of the positron experiment is complicated because the positron wave function and the perturbation of the electron by the positron are not known.

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TABLE I. Values of $J(z)$ and $f(k)$ for the two valence electrons in LiH. The values obtained by subtracting the calculated $1s^2$ core contribution from $J(z)$ measured along three crystallographic directions are given in the upper portion of columns 2–4. (The average of these is given in column 5.) The experimental uncertainty in J for each direction is ± 0.02 a.u.$^{-1}$ for $0 \leq z \leq 1.8$. The measured scattering factors (two electrons per H atom) from Ref. 1 for the first five Bragg peaks are given in the lower portion of column 5. (The effects of thermal motion have been removed using a Debye-Waller coefficient $B = 1.8$.) The error quoted is <0.01 for all entries. In columns 6 and 7 values of $J(z)$ and $f(k)$ calculated from the model described in the text are given for two sets of values of the parameters. The energy E_0 (in atomic units) represents the energy of the central ion plus the Coulombic interaction energy that would result if the central ion were a point charge. The $J(z)$ curves corresponding to columns 6 and 8 are shown in Fig. 1; the parameters obtained by Hurst (Ref. 1) for his open configuration are used for column 8. No allowance for thermal motion has been made in the calculated $f(k)$. The $J(z)$ values in column 7 are averages over the three crystallographic directions.

	Experimental valence electron $J(z)$				Calculated valence electron $J(z)$		
z(a.u.)	[100]	[110]	[210]	Av.	$\alpha=0$ $a=1.16$ $E_0=-0.70$	$\alpha=0.60$ $a=0.94$ $d=1.5$ $E_0=-0.37$ [Eq. (4)]	$\alpha=0$ $a=0.57$ $b=1.01$ $E_0=-0.93$ (Hurst)
0	1.49	1.44	1.48	1.47	1.46	1.45	2.32
0.2	1.35	1.41	1.41	1.39	1.34	1.28	1.83
0.4	1.09	1.14	1.10	1.11	1.04	0.91	1.02
0.6	0.79	0.77	0.75	0.77	0.72	0.57	0.50
0.8	0.44	0.45	0.46	0.45	0.46	0.34	0.24
1.0	0.24	0.22	0.26	0.24	0.28	0.20	0.12
1.2	0.12	0.11	0.12	0.12	0.16	0.12	0.07
1.4	0.07	0.07	0.07	0.07	0.10	0.07	0.03
1.6	0.04	0.05	0.05	0.05	0.06	0.04	0.01
1.8	0.03	0.03	0.04	0.03	0.04	0.02	0.01
	Experimental valence electron $f(k)$				Calculated valence electron $f(k)$		
$(\sin\theta)/\lambda$	hkl						
0.212	111			0.62	1.07	0.61	0.62
0.245	200			0.52	0.90	0.57	0.47
0.347	220			0.27	0.51	0.19	0.22
0.406	113			0.14	0.36	0.16	0.14
0.424	222			0.12	0.33	0.07	0.13

The Hurst wave function for the H$^-$ ion was chosen to be spherically symmetric about the H nucleus. An attempt was made to introduce the effects of an anisotropic charge density by mixing in some doubly degenerate d-like function, which points toward the six nearest neighbors. The function chosen for the two electrons on the H$^-$ ion was a singlet determinant composed of

$$\begin{aligned}\psi_1(r_1) &= [\pi^{-1/2}/(1+\alpha^2)^{1/2}][a^{3/2}e^{-ar_1} \\ &\quad + (i\alpha/\sqrt{6})d^{7/2}r_1{}^2e^{-dr_1}\sin^2\theta_1\cos 2\varphi_1], \\ \psi_2(r_2) &= [\pi^{-1/2}/(1+\alpha^2)^{1/2}][a^{3/2}e^{-ar_2} \\ &\quad + (i\alpha/3\sqrt{2})d^{7/2}r_2{}^2e^{-dr_2}(3\cos^2\theta_2 - 1)],\end{aligned} \tag{4}$$

where α determines the relative amount of d character. For $\alpha=0$ and $a=0.77$, Eq. (4) reduces to Hurst's closed configuration with minimum crystal-field energy.^{2} The parameters a, d, and α were adjusted to give a best fit to both the Compton-profile and x-ray scattering-factor measurements. The best values of the parameters found ($\alpha=0.6$, $a=0.94$, and $d=1.50$) do not give satisfactory agreement with both measurements. Furthermore, for that choice of parameters which minimizes the discrepancy between the measured and calculated Compton profile ($a=1.16$, $\alpha=0$), the discrepancy between the measured and calculated scattering factors is very large. The results are summarized in Table I. A further attempt to improve the wave function was made by orthogonalizing the H$^-$ ion function to the Li $1s$ function, but this produced no improvement in the calculation.

The anisotropy found in the Compton profile (see Table I) is small and was not measured with sufficient statistical accuracy or for enough crystal orientations to allow the determination of a unique model of the momentum-density asymmetry. A transfer of some momentum density at $z \sim 0.5$ a.u. in the $\langle 111 \rangle$ directions to a torus around the $\langle 100 \rangle$ directions at $z \sim 0.7$ a.u. qualitatively yields the anisotropic features of the three measured $J(z)$ curves. The calculation which includes some d character presented in the table qualitatively yields the measured anisotropy at $z=0$.

CONCLUSIONS

The large differences in the Compton profile between the experiment and the various calculations reflect the sensitivity of the Compton measurements to the valence-electron wave functions. It appears that a fairly detailed band calculation will be necessary to obtain agreement with the Compton-profile measurements, the x-ray scattering-factor measurements, and the crystal cohesive energy.

ACKNOWLEDGMENT

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