	Experiment title: Exciton Mapping in LiF	Experiment number: HE-928
Beamline: ID16	Date of experiment: from: 6-12-00 to: 12-12-00	Date of report:
Shifts: 18	Local contact(s): Abhay Shukla, Jean-Pascal Reuff	<i>Received at ESRF:</i>
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Report:

The purpose of this study was to probe the spatial structure of the valence exciton in LiF by looking at its energy, line shape, and oscillator strength at high \mathbf{q} . In inelastic x-ray scattering one measures $S(\mathbf{q}, \omega) = \text{Im}[\chi(\mathbf{q}, \omega)]$, where $\chi(\mathbf{q}, \omega)$ is the fourier transform of the density-density greens function, $-i\langle 0|T[\pi(\mathbf{x}, t)\rho(\mathbf{x}', t')]|0\rangle$. For independent electrons this quantity has the explicit form

$$S(\mathbf{q}, \omega) = \sum_{if} \left| \int \psi_f^*(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \psi_i(\mathbf{r}) \right|^2$$

which is formally identical to the expression for the structure factor in x-ray crystallography, with the exception that the sum is on all *transitions* rather than on all occupied states. In other words, it is possible - at least theoretically - to reconstruct the spatial structure of an *excitation* with IXS using crystallography methods, the primary difference being that in crystallography one probes the charge density whereas here we are talking about probing the *transition* charge density. The catch is that the ground state charge density is unique whereas there are many excited states, so this technique can only be used when a single excited state can be isolated (a rare occasion!).

For the specific case of excitons [for which the above expression must be generalized to the two-body case, involving a slater determinant on one side and an atomic configuration on the other] this is possible because the exciton band is energetically resolved from all other excited states. The only degeneracy in the problem is that excitons of different momenta overlap, however they can be distinguished in a momentum-resolved experiment. The proposal, therefore, was to measure energy-loss spectra of the valence exciton in LiF at a fixed reference point \mathbf{k} in many brillouin zones, i.e. $\mathbf{q} = 2\pi/a (h, k, l) + (k_x, k_y, k_z)$ for as many values of (h, k, l) as achievable. The data set would be the mod squared of the transition charge density of the valence exciton with momentum \mathbf{k} , which could be inverted - modulo the normal phase problems in x-ray scattering - to achieve the exciton wave function at that particular \mathbf{k} point. This could be done, in principle given enough beam time, for the entire brillouin zone to fully map the exciton band in real space.

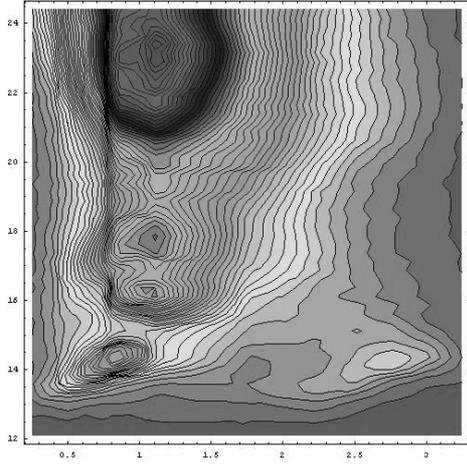


Figure 1: $\mathbf{q} = h \frac{2\pi}{a} (1,0,0)$

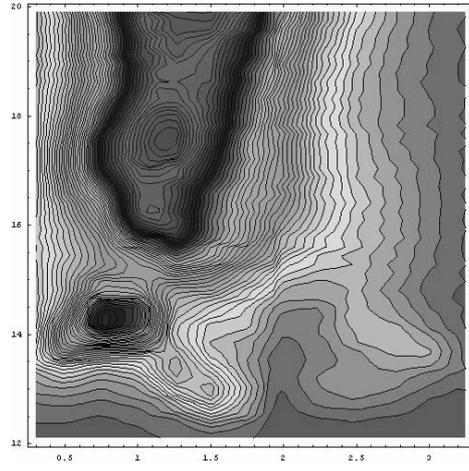


Figure 2: $\mathbf{q} = h \frac{2\pi}{a} (\cos(15^\circ), \sin(15^\circ), 0)$

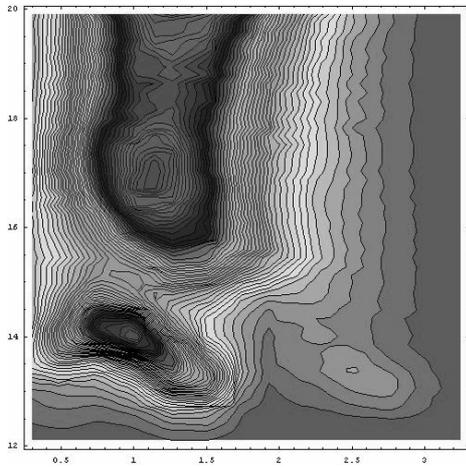


Figure 3: $\mathbf{q} = h \frac{2\pi}{a} (\cos(30^\circ), \sin(30^\circ), 0)$

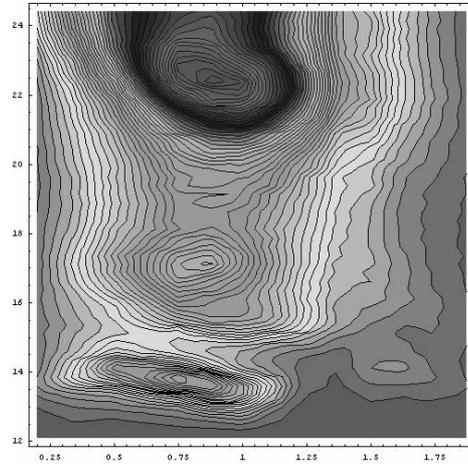


Figure 4: $\mathbf{q} = h \frac{2\pi}{a} (1,1,0)$

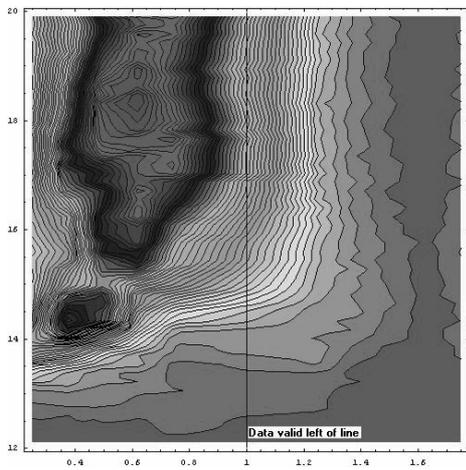


Figure 5: $\mathbf{q} = h \frac{2\pi}{a} (1,1,1)$

For reasons which are still not entirely clear to me, we chose to deviate from the proposed experiment and just measure the exciton dispersion with very fine \mathbf{k} steps along a few high symmetry directions in the reciprocal lattice. Owing to the improved experimental configuration we had typically 100 Hz in the exciton peak in the loss spectra and were able to generate the impressive set of raw data, Figures 1-5, shown above. While the original analysis proposed is not possible on this data set [perhaps that can be revisited in a future experiment], there are still many useful things one can say:

1. From careful fitting, it has been determined that in the limit $\mathbf{q} \rightarrow 0$ the (100) spectra (Fig. 1) show a clear q^2 dependence. This means that the exciton is dipole-allowed at $\mathbf{q}=0$, which means that its overall symmetry is P , or in cubic point group notation it is t_{1u} . Were it an exciton of, for example, D symmetry it would have a q^4 dependence.
2. From tight-binding calculations of the band structure the predominant symmetry near the valence band maximum is t_{1u} , whereas near the bottom of the conduction band it is a_{1g} . Therefore when one turns on an electron-hole interaction one expects the first bound state to be of $t_{1u} \otimes a_{1g} = t_{1u}$ symmetry, consistent with the experiment.
3. Tight binding calculations show that the F 2p valence band has a much higher effective mass than the Li 2s conduction band. So one can probably think of this object as a spin-0 bound state of a F 2p hole and an electron in a linear combination of surrounding 2s levels with S symmetry.
4. The fine \mathbf{k} -steps revealed something new: The exciton has zero oscillator strength in certain regions of reciprocal space. An ideal frenkel exciton with no internal structure would be visible everywhere. In other words, because of its internal symmetry there exist certain wave vectors at which the exciton *simply cannot modulate the charge density*. This is not really unexpected since it just means the exciton exhibits extinction rules, i.e. form factor effects, which is what we were originally after. In fact, an extinction rule one a priori expects is that the exciton to have zero oscillator strength at $q=0$, which is required since it is electrically neutral. Still, I think it is pretty cool that you can see this.

Future experiments on this system, in particular Abhay's high pressure measurements, are likely at ID16. The greatest current experimental limitation there is the pump which is connected to the arm of the ~ 100 meV setup in the monochromator hutch. It makes movement of the arm past 90 degrees impossible. Kinematically it is possible to extend the above scans by 40% in \mathbf{k} , which would bring about corresponding increases in spatial resolution.