ESRF	**Experiment title:** Band and Exciton Dispersion in Cu Halides Measured with Resonant Inelastic X-ray Scattering	**Experiment number:** HE-690
Beamline: ID16	**Date of experiment:** from: 08-09-1999 to: 14-09-1999	**Date of report:** 23-02-2000
Shifts: 18	**Local contact(s):** Abhay Shukla	*Received at ESRF:*

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Report:

This experiment could not be called either a success or a failure, as it went in directions we did not anticipate. Our objective was to measure the **q**-dependence of the interband transitions and valence excitons at the Cu K edge in CuCl (and, time permitting, CuBr and CuI) to learn something about (1) exciton dispersion and (2) coherence and momentum conservation in Resonant Inelastic X-ray Scattering (RIXS). We expected the signal from CuCl to be very large, owing to its zincblende structure which assures dipole-allowed transitions at all points in the Brillouin zone.

To our surprise we saw no Raman effect in CuCl at all. The alignment and signal were both excellent. The fluorescence yield measurements showed a nice edge feature [Figure1].

We had ~10^{12} photons/sec in our 100 meV beam with energy resolution in resonant geometry of **ΔE=217 meV** (this could have been improved but it was not deemed practical at the time). We attempted many incident energies across the Cu K edge [Figure 1] but never saw any inelastic scattering.

We checked the alignment of our spectrometer by placing a piece of aluminum foil in the sample position and measuring the plasmon. We did so both by keeping the analyzer fixed and scanning the incident energy, and then by fixing the incident energy and scanning the analyzer. In both cases we saw a plasmon at 18 eV energy loss [count rate=8 Hz in the peak]. We concluded that there were no problems with our instrument. We therefore are comfortable making the following statement:

> *There is no Raman effect in CuCl like that seen previously in the transition metal oxides NiO* [1], *Nd_2CuO_4* [2], *La_2CuO_4* [3] *and $Sr_2CuO_2Cl_2$* [3].

We have explored many candidate explanations for this and have so far rejected them all. Note that we did not attempt to look at the direct d-band emission, as has been seen from pure Cu metal, which becomes Raman-like below threshold [4].

At this point we still had *four more days of beam time*, and no idea what to do, so we started wandering around the labs looking for something to put in the beam. We finally came up with Abhay Shukla's LiF crystal, which according to Kittel had a 10 eV band gap and an exciton with a binding energy of 1 eV. It seemed loosely related to the original proposal (*c.f.* exciton dispersion) and he had planned on looking at it anyway, so why not?

LiF turns out to have a huge Raman effect, i.e. in the nonresonant channel [Figure 2]. The band gap is actually closer to 14.5 eV, and the exciton disperses beautifully, with its own periodicity rather than the periodicity of the lattice (indicating that most of its mass comes from internal coulomb interactions, which result in a non-periodic form factor, rather than textbook wave function hybridization).

In addition, LiF develops defects when exposed to ionizing radiation in the form of atoms displaced from their lattice position into an interstitial site. These defects, which can be called F-centers or color centers, have electronic transitions in the 1.3 eV range, which makes the material absorbing to red light and gives it a yellow or orange color, depending upon the exposure time. We were able to measure this absorption band, i.e. in the dielectric constant via the loss function $-\mathrm{Im}1/\varepsilon(q,\omega)$. This absorption band, and its time dependence in units of beam exposure time to the beam, is shown in Figure 4.

[1] C. C. Kao, *et. al.*, Phys. Rev. B, **54**, R16361 (1996)
[2] J. P. Hill, *et. al.*, Phys. Rev. Lett., **80**, 1967 (1998)
[3] P. Abbamonte, *et. al.*, Phys. Rev. Lett., **83**, 860 (1999)
[4] A. Kaprolat, *et. al.*, (unpublished?)

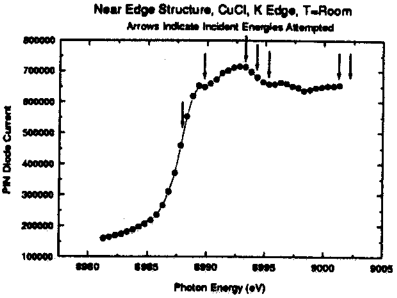

Figure 1 - Near edge structure of CuCl and incident energies attempted (red arrows).

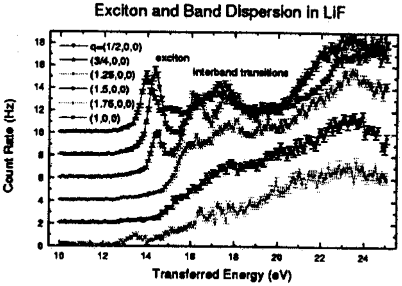

Figure 2 - Loss function of LiF. Interband transitions start at 15.5 eV. The binding energy is about 1 eV.

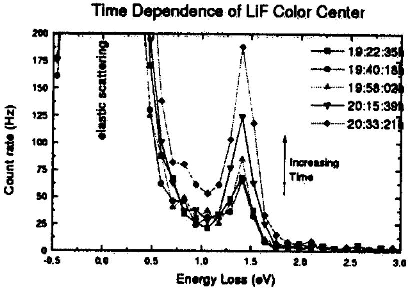

Figure 3 - Time evolution of the exciton band in LiF. Oscillator strength builds as the crystal is exposed to the beam.