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# INELASTIC SCATTERING ENERGY LOSS IN CAF2 OBSERVED WITH SOFT X-RAY FLUORESCENCE SPECTROSCOPY

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# Inelastic Scattering Energy Loss in $CaF_2$ Observed with Soft X-ray Fluorescence Spectroscopy

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## Abstract

The advent of third generation synchrotron radiation sources has stimulated interest in the study of X-ray emission using photon excitation. Soft x-ray fluorescence (SXF) provides a mean of measuring the element and angular momentum selective valence band density of states in complex materials. Tenability of the excitation source allows a detailed investigation of the dynamical behavior of the relaxation channels and the coupling between the excitation and emission process that occurs near a resonance or an absorption edge. As an example of resonant inelastic scattering studies in solid systems by SXF spectroscopy at the insertion device beam line BL 8.0 at ALS, results from $CaF_2$ will be presented. When the energy of exciting photons is tuned to the Ca 2p-3d threshold absorption peak in $CaF_2$, the SXF produced by recombination of the excited electrons with core holes exhibits remarkable resonance's for both the $2p_{3/2}$ and $2p_{1/2}$ levels. When the resonant 2p-3d SXF peaks are excited, additional broad peaks appear in the spectra below the normal valence band spectrum, which are displaced from the resonant peaks by about 17 eV and track the changes in excitation energy. We identify this as evidence of a coherent, inelastic scattering process, analogous to resonant Raman scattering, in which incident photons excite a localized electronic transition and are re-radiated at an energy reduced by the energy of the excitation. Evidence is also presented which indicates that the 2p-3d absorption transitions lie about 1 eV above a weak Ca 4s absorption threshold.

## 1.Introduction

Soft X-ray fluorescence spectroscopy using photon excitation has a number of unique properties. Photons penetrate many atomic layers into the material, so that it is a true bulk probe of the electronic structure, which is less affected by surface contamination than electron spectroscopy. Since a core hole of well defined angular momentum is generated by a dipole transition in SXFS, the method is site and angular momentum selective. Thus SXFS measures the angular momentum selected local partial density of states (LPDOS) for each constituent of a material. Traditionally, this technique has been limited by low fluorescence yields and relatively weak soft x-ray excitation sources. With the advent of third generation synchrotron radiation sources, many new experiments have now become feasible.[1,2]

The X-ray absorption spectrum at the Ca L edge in $CaF_2$ shows sharp features near the absorption edge[3] associated with Ca 2p - Ca 3d transitions. The 2p - 3d transitions are much stronger than the other dipole allowed transition, 2p-4s, because the Ca 3d orbitals are very localized and involve many electrons. Using tunable synchrotron radiation, several workers have found that the excitation to the 3d bound states have a dramatic influence on Auger and other de-excitation processes, as a result of the excited electrons acting as spectator electrons during the decay process[2,4]. Electrons excited to these bound 3d states can also decay through radiative recombination with the 2p core holes, resulting in fluorescence, which is the principle subject of this paper. In this letter, we report the soft X-ray fluorescence (SXF) measurements of the Ca L valence spectra of $CaF_2$ excited at the Ca L edge. The SXF spectra have the same initial states as Auger but a one-hole final state, so that the complication of correlation effects between the final state holes is eliminated. Thus new information can be obtained by carefully measuring the fluorescence spectra as the excitation energies are stepped through the Ca L edge, as shown by Rubensson et al.[4]

The de-excitation process in B K emission spectra with excitation to the B 1s core exciton at the boron K edge has recently been investigated[4,5] in h-BN [4] and $B_2O_3$. The electron screening of the spectator electron was found to be responsible for an energy shift of the valence band emission spectrum. The final state of the "spectator" fluorescence transition is thought to be a valence exciton. But other final states are possible. The spectator electrons may be promoted into the conduction band as in a shake-up process, thus satellite or broadening are expected to show in core level spectroscopy.

## 2. Experiment

The experiment was performed on beam line 8.0 at Advanced Light Source (ALS) which consists of an 89 period, 5 cm undulator and a spherical grating monochromator. The SXF spectra were measured using spectrometer[7] consists of an ultrahigh vacuum sample chamber and a Rowland circle grating spectrometer. The fluorescence spectrometer has a fixed entrance slit, four spherical diffraction gratings and a position sensitive area detector. The gratings are interchangeable from outside the vacuum. The detector is a true photon counting device utilizing micro-channel plates and a resistive readout anode.

Fluorescence spectra are measured by positioning the detector along the Rowland circle to intercept the spectrum of interest, and utilizing the area detector to record the entire spectrum simultaneously. Scanning is accomplished by a precision X-Y-θ table on which the detector chamber is mounted. Both detector scanning and data acquisition are automated through an IEEE-488 bus interfaced to a personal computer.

All measurements reported here were made with a 100 μm entrance slit for the spectrometer. The spectra were obtained with a 1000 lines/mm, 10 meter radius grating. At the Ca $L_{2,3}$ spectral region, the resolution of the spectrometer is approximately 1.0 eV. The energy resolution of the monochromator was set to be 0.3 eV during these measurements. Sample radiation damage was a concern, but we observed no change in the spectra or physical appearance of the sample during the 10 minute time required obtaining a single spectrum. Fresh spots of the sample were used for each new scan.

**3. Results and Discussions**

In Fig.1, the Ca $L_{2,3}$ emission spectra of $CaF_2$ for excitation energy varying from 346.0 eV to 359.0 eV are shown. The numbers labeling the curves are the photon energies of the excitation photons. Sharp elastic peaks with varying intensity were observed in these spectra for excitation energies above 347 eV. These recombination peaks show strong resonance's at both the $L_3$ ($2p_{3/2}$) and $L_2$ ($2p_{1/2}$) edges with intensities much greater than the main emission feature. The intensity of these resonance peaks falls off when the excitation energy is changed by about one electron-volt. In Fig. 2. A full view of the on-resonance spectra excited at 349 and 352 eV photon energies are presented.

In Fig. 1, a narrow emission peak at 337 was observed for all excitation energies. This feature remains unchanged until the onset of the second 2p - 3d resonance, when the intensity of the high energy side increases to give it an asymmetric look. This peak represents the normal valence band x-ray emission spectra. The asymmetric broadening results from the superposition of $L_3$ and $L_2$ spectra. It is significant that this peak is excited below the onset of the 2p-3d resonance transition. This provides strong evidence that a 2p-4s excitation threshold lies several eV below the 3d resonance, and that a complete description of the absorption spectrum must include the influence of the Ca 4s states.

The most surprising part of these spectra appears below the 337 eV feature. At an excitation energy of 346 eV, the spectrum is clean without a trace of an elastic peak. When the excitation energy is increased by one eV, a broad spectral feature with a peak centered at about 330 eV is observed. The intensity of this spectral feature reaches its maximum value relative to the valence band spectrum, when the excitation energy is 349 eV, coinciding with the maximum excitation of the elastic recombination peak. A similar broad feature appears for the $L_2$ edge as well, which is about 3 eV above the $L_3$ edge. At an excitation energy of 350 eV, this feature shows up on the lower energy shoulder of the 337 eV peak. The peak position of this feature can be approximately identified just above 333 eV. Again this broad spectral feature achieves its maximum intensity when the $L_2$

elastic recombination peak is at resonance, and disappears for excitation energy of 353 eV and above.

The resonance of the elastic peak is well understood. The 3d states of Ca ions in $CaF_2$ remain very much localized. When monochromatic photons are tuned to excite Ca 2p core electrons into 3d states, the subsequent recombination of 3d electrons with core holes gives the large resonance's in a resonant elastic scattering process. Similar resonance processes have been observed in the K spectra of a number of boron compounds, where 1s core electrons are excited into $p\pi^*$ localized unoccupied states.[6,8]

In highly ionic compounds like $CaF_2$, the valence band is derived largely from fluorine 2p atomic orbitals.[9] The observation of the spectral feature at 337 eV is an evidence for electrons of s (or d) symmetry in the valence band. In the description of x-ray spectra based primarily on atomic orbital model, such a feature might be described as a "crossover" transition from the F 2p orbitals. It is probably better understood from a band structure calculation which properly includes the effects of bonding and symmetry. The energy position of this feature falls within the valence band energies determined by other measurements. Tiedje et al.[3] obtained binding energies of 348.9 eV and 8.0 eV for the $2p_{2/3}$ core hole and the top of the valence band. That would give a high energy limit of 340.9 eV for the valence band emission. Inspecting our spectrum excited with 346 eV photons, which produces an $L_3$ normal x-ray fluorescence spectrum, uncontaminated by resonance features and the $L_2$ spectrum, the spectral features are mostly concentrated below 338 eV with a weak shoulder extending to about 340. The discrepancy in the spectral maximum could be due to a reduced contribution of s-like electrons at the top of the valence band, or possible to instrumental errors. But in any case it is clear that most of the s-like character of the spectrum is concentrated within 3 eV of the low energy region of the observed spectrum.

Valence band photo emission by Poole *et al.*[10] yields a band width of 5 eV. Our data show intensity contribution between 335 eV and 340 eV, even though the intensity is mostly below 338 eV. The photo emission spectrum was dominated by fluorine p-type states, while our suggest that the s type states exist near the Ca ions. Calculation by Heaton and Lin[8] gave a bandwidth less than 4 eV with mostly fluorine p character for valence states (more than 97%). Our data seem to agree with photo emission measurement in terms of bandwidth. They also indicate an s contribution at the Ca site, which is concentrated at the bottom of the band with a weak extension toward the band maximum.

The x-ray absorption spectra of $CaF_2$ have been successfully described in terms of an atomic orbital model, which incorporates the spin-orbit splitting of the 2p core levels and the spin-orbit and crystal field splitting of the empty 3d levels.[11] On the basis of this model, it has been claimed that the Ca 4s states that contribute to the bottom of the conduction band play no role in the determination of the absorption spectra. Further, it has been suggested that at threshold excitation, 3d states that are bound by as much as 3 eV with respect to the conduction band edge, presumably due to configuration interactions with the core hole will shift the 3d states down into the band gap. The

excitation of the valence band spectra at energies about 3 eV below the 3d resonance's strongly indicates that the conduction band edge is s-like and lies about 3 eV below the peak of the d-band resonance, in clear disagreement with both of these assertions.

The broad peak appearing below the valence (normal) emission is not present when the excitation is well off the 2p -3d resonance. We believe that this peak results from a third de-excitation channel to the two that are usually identified. For resonant excitation, two channels for radiative de-excitation are usually identified. In the first de-excitation channel, the excited electron recombines directly with the core hole, producing the resonant elastic peak. In the second channel, the core-hole may be annihilated by a valence electron, giving rise to valence emission at about 337 eV, with the electron in the 3d states acting as a spectator. The spectator electron will subsequently change its electronic state, since a localized 3d state without the core hole will be more weakly bound and will increase the energy. In $CaF_2$, this transformation is apparently accomplished without an energy shift because the 3d states lie above the conduction band threshold and are therefore resonant with delocalized states. In boron compounds, the presence of the spectator electron in a bound state provides screening, which results in a shift of the valence band spectrum by the amount of the binding energy of the core exciton minus the binding energy of the valence exciton[4]. We observe no measurable energy shift or change in shape in the normal valence band emission spectrum at the 3d resonance's, other than the appearance of $L_3$ emission, which is consistent with other evidence that the 3d resonance's are resonant with conduction band states.

The broad energy-loss feature below the valence band provides evidence for a third de-excitation channel, which involves a resonant inelastic scattering process analogous to resonant Raman scattering. In this two electron process, resonantly excited electrons excite an electronic transition from the valence to conduction bands before recombining with the core hole, and produce emission spectra whose energy is reduced from the x-ray excitation energy by the energy of the second electronic excitation. The energy difference between the elastic and inelastic peaks indicates that the electronic excitation has a value of about 17 eV. The obvious candidate for this strong, local electronic excitation is the 2p-valence band to 3d conduction band transition. The separation of the normal valence band spectrum and the resonant peak provides a measure of the position of the 3d states with respect to the valence band in the presence of the core hole. The separation between the elastic and inelastic peaks provides a measure of the energy separation without the core hole. With this interpretation, the energy separation of 6.5 eV between the normal valence band spectrum and the inelastic peak provides a measure of the binding energy of the 3d states by the core hole. We can note that this interpretation is somewhat analogous to the previous discussion for boron compounds, except that here the normal spectrum and the energy shifted spectrum appear together and result from de-excitation via competing channels.

To better examine this, we display the difference spectra in Fig. 3 (normalized to equal height for the 337 eV peak). The 346 eV spectrum is subtracted from all spectra excited at 347 eV and above. The difference spectra are re-plotted with labels of (a) through (i). It's evident that there are two groups of energy loss features. The feature at

about 331 eV in curves (a) through (d) corresponds to the $L_3$ excitation. There is an energy shift of 1 eV between the structure and structure in curve (d), which is on resonance. The cause for this shift is not understood at this time. The difference curve of (e) through (d) show energy-loss features for the $L_2$ edge, which is about 3 or 4 eV higher in energy. The curves (f) through (i) also have a feature at about 338 eV, increasing in intensity with excitation energy. We believe that this is the valence band emission to the $2p_{1/2}$ core levels.

The energy separation between the recombination peak and the energy-loss structure roughly agrees with $CaF_2$ band structure calculations. If the scattering by the valence electrons is true, these electrons have to be promoted to the states with a p-character, obeying the dipole selection rule. In calculations by Heaton and Lin[9] the lowest conduction band states with Ca p orbital contribution is found to be at $\Gamma_{15c}$ point, about 21 eV above the valence band $\Gamma_{15v}$ point, where the density of states is the largest. The separation in our data between the excitation photons and the energy-loss feature below the main emission feature is around 19 eV. Considering the assumptions used in the LCAO band structure calculations, in our opinion the agreement is good.

These energy-loss structure appear to be much wider, compared with the valence band. This is probably consistent with the fact that the Ca p-type conduction band states are broad. If these energy-loss features are resulting from the inelastic scattering of the valence electrons, the width of the energy-loss feature is a convolution of the valence states and the Ca p-type conduction band states widths.

The energy-loss appearance seems to be closely related to the localization factor of the excitation. We recently measured the x-ray fluorescence at the Ca $L_{2,3}$ edge of CaSi and $CaSi_2$.[12] The energy-loss feature was present for the CaSi spectra, but not for $CaSi_2$. The Ca 3d states are more localized in CaSi than in $CaSi_2$, as evidenced by the ratio of recombination peaks and main emission features from the valence band.[13] The extra silicon concentration in $CaSi_2$ obviously increased the interaction of the Ca d orbitals with delocalized Si s- and p- orbitals. The resonant elastic recombination was strong in CaSi, and similar energy-loss structures were also present below the valence band emission for CaSi. But since there is no detailed band structure calculation was available for CaSi, it was not possible to confirm whether the separation between s-type of Ca valence states and p-type Ca conduction band states agrees with our measurement.

In conclusion, we have measured the Ca $L_{2,3}$ fluorescence of $CaF_2$. The s-type valence electronic states around Ca yield a width comparable to photoemission. The localized excitation of Ca 2p - Ca 3d produces resonant recombination peaks. Prominent energy-loss features observed below the valence emission and the valence electron scattering to the recombination photons are believed to be the cause for such energy loss.

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Figure Captions

1. The stack plot of the Ca $L_{2,3}$ emission of $CaF_2$. The numbers on each curve indicate the excitation energy from the monochromator, and the dashed curves are when the excitation hit the resonance.
2. The full view of the Ca $L_{2,3}$ emission spectra for both $L_2$ and $L_3$ edge at the resonant condition.
3. The difference spectra of the Ca $L_{2,3}$ emission spectra. The curves are obtained by subtracting the 346 eV excited spectrum from all other spectra in Fig.1.

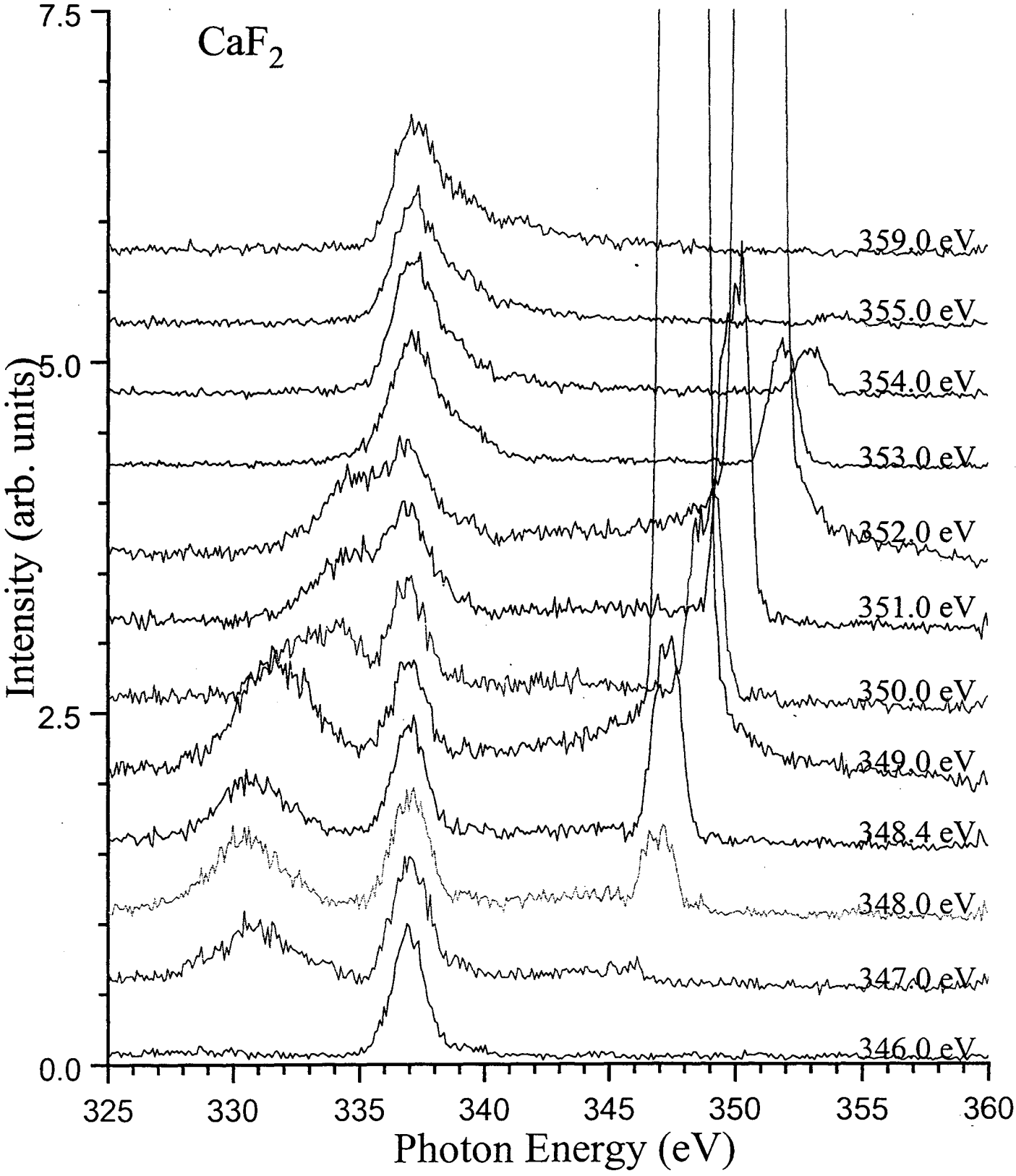
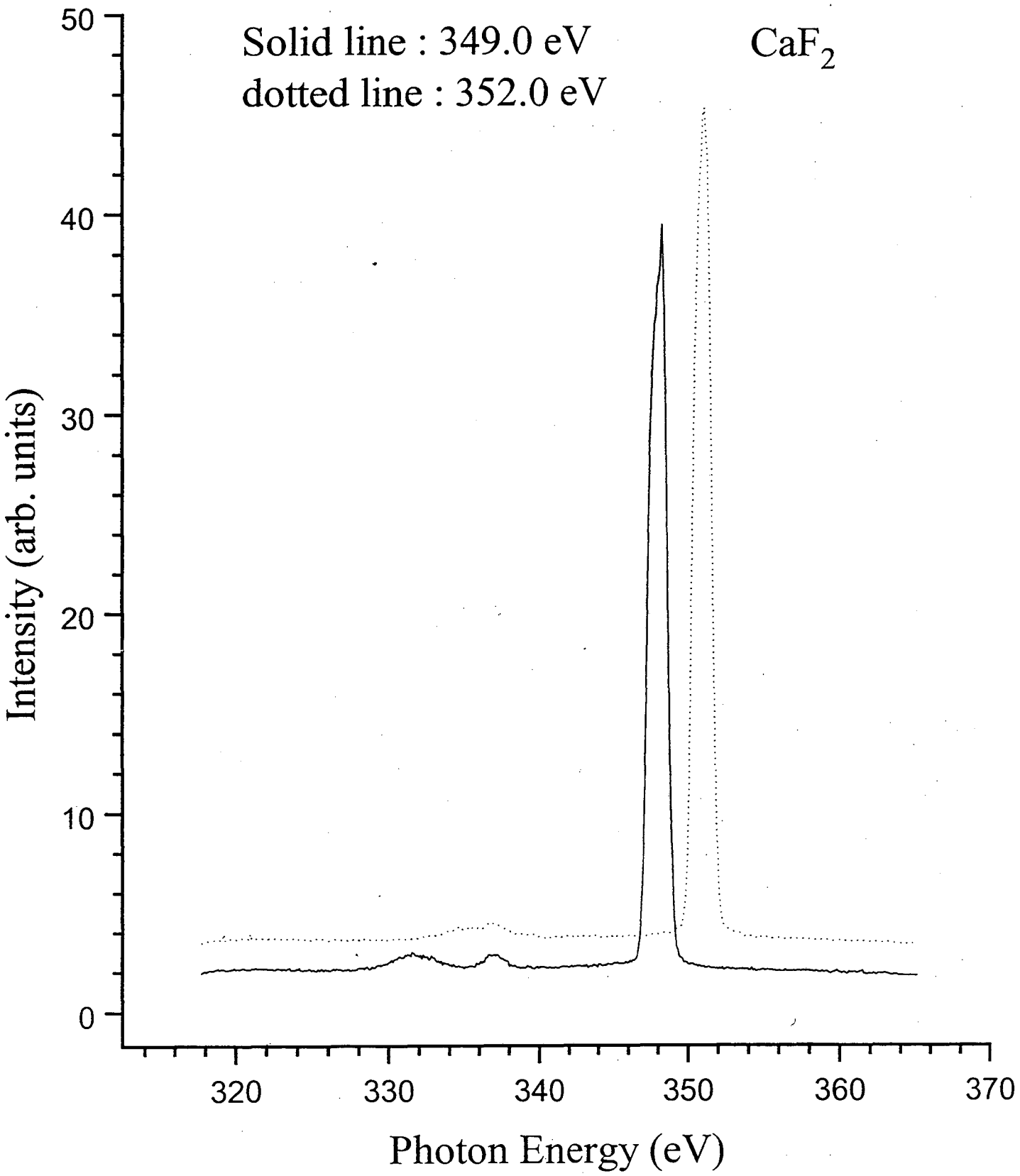

CaF2
7.5
5.0
2.5
0.0
Intensity (arb. units)
325
330
335
340
345
350
355
360
Photon Energy (eV)
359.0 eV
355.0 eV
354.0 eV
353.0 eV
352.0 eV
351.0 eV
350.0 eV
349.0 eV
348.4 eV
348.0 eV
347.0 eV
346.0 eV

Fig. 1


Solid line : 349.0 eV
dotted line : 352.0 eV
$CaF_2$
Intensity (arb. units)
Photon Energy (eV)
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10
20
30
40
50
320
330
340
350
360
370

Fig. 2

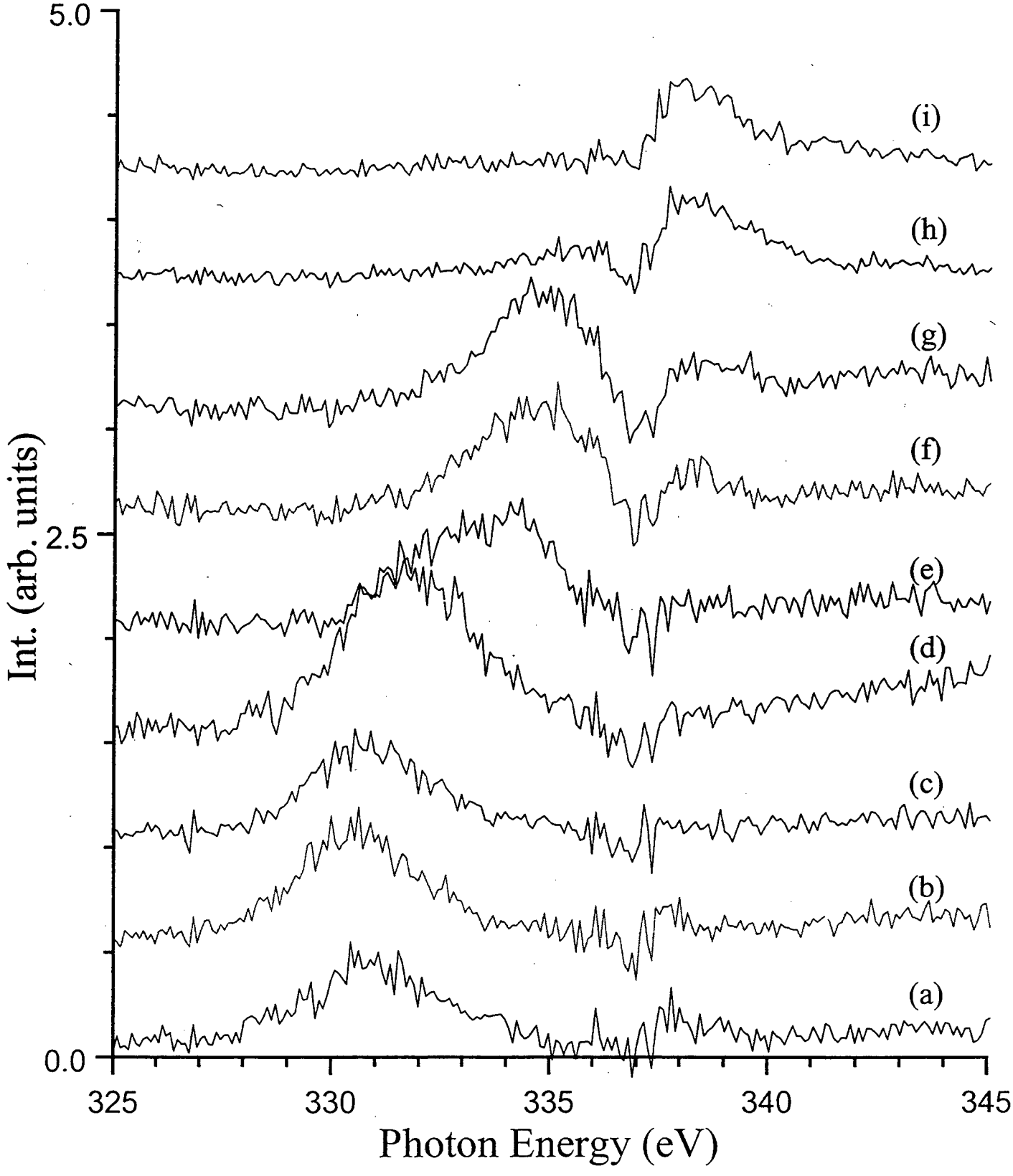
5.0
2.5
0.0
Int. (arb. units)
(i)
(h)
(g)
(f)
(e)
(d)
(c)
(b)
(a)
325
330
335
340
345
Photon Energy (eV)

Fig. 3

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