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Cu L_3 core-hole effects in the x-ray absorption of CuCl

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Core-hole effects are studied through Cu L_3 x-ray-absorption experiments on CuCl. This spectrum is compared with the calculated density of states, the photoemission, the bremsstrahlung isochromat spectroscopy, and optical spectra. From this comparison it is concluded that the lowest energy structure in the x-ray-absorption spectrum cannot be explained on the basis of one-electron density of states where the presence of the core hole is not taken into account, but it is more like a metastable excitonic state lying in the continuum.

I. INTRODUCTION

Cuprous halides appear as prototypes of compounds with valence excitons. On these compounds a great number of studies have been performed: not only the observation and characterization of the excitons by their binding energies and their oscillator strengths,[1] but also the study of properties such as fine structure and various interactions with phonons,[1] impurities,[2] excitons,[3] etc.

One of the peculiarities of valence excitons in cuprous halides is the heavy-hole mass due to the important contribution of $3d$ Cu orbitals to their wave functions. The lowering of this contribution from CuCl to CuI (Ref. 4) is accompanied by the lowering of the binding energy[5] of these valence excitons in the respective cuprous halides.

This behavior of valence excitons in cuprous halides shows some analogy to that of the core exciton, where the infinite effective mass of the hole leads to its localization on the excited site during its lifetime. In this paper we are interested in excitons for which the hole lies in Cu L_3 level. In the conventional configuration, according to the dipole approximation, the excited electron state is in the $4s$ Cu conduction band. Hence, if an exciton is created, its characteristic absorption line will appear below the conduction-band minimum (CBM) and will not mix with absorption maxima due to density-of-states (DOS) structures. However, as we have shown recently by linear-muffin-tin-orbital (LMTO) calculations and bremsstrahlung isochromat spectroscopy (BIS) experiments,[6] the contribution of d orbitals in the lower conduction bands is not negligible. Hence we have also to see if core-hole gives rise to excited state like metastable excitons when the final states are in d orbitals. The aim of this paper is to see if the core exciton in CuCl involves the s orbitals or the d orbitals. In the first case the exciton line will fall in the forbidden gap, whereas in the second case it may fall even above the CBM.

Generally, it is observed that the binding energy (E_b) of core excitons is greater than that of valence excitons. An extensive study[7] summarizes typical experimental values involving $3d$ excitons in III-V compounds and $3p$ excitons in II-VI compounds. For the $2p$ core exciton in Si, there are some discrepancies in its binding energy, due in part to the steplike shape of the experimental feature and also to surface effects. A typical value, 0.3 eV, of E_b in Si is about 20 times larger than 0.015 eV for the corresponding valence excitons.[8,9] The screening effect by valence excitons may be the origin of the much higher value of E_b for core excitons.[10] Some theoretical approaches are proposed to take into account these dynamic effects of valence excitons, through the polaron model, to describe the wave function of core excitons. For CuCl, such calculations give $E_b = 1$ eV when positive and negative polarons are considered to be delocalized.[11] For the same compound, in an alternative approach where the hole polaron is considered as localized due to its infinite mass, E_b is found to be 0.79 eV.[12]

According to these considerations the characterization of a core exciton is made in two steps: first, one verifies if the experimental structure is a DOS feature; if not, one evaluates E_b. This implies that one can determine the minimum of the conduction band in the energy scale of the x-ray-absorption (XAS) spectrum with an accuracy compatible with the order of magnitude of E_b. Formally, knowledge of the gap gained through excitonic spectroscopy, and of the position of the valence-band maximum (VBM) with respect to the core level gained through photoemission and the position of the core excitonic feature in the energy scale of the XAS, give the binding energy E_b.

However, the experimental errors involved in this procedure may be important; often they are of the order of the magnitude of E_b.[8] The most important error arises from the difficulty in determining the exact position of the VBM, with respect to the core level, by photoemission experiments. These measurements are made difficult by surface effects and by the poor precision when the VBM is identified as the beginning of the electron distribution curve (EDC). In the present case the difficulty is enhanced by the high-energy measurements inherent in

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the Cu $2p_{3/2}$ level in regard to the majority of the studies devoted to excitons where the core hole lies in an energy level about 100 eV below the VBM.[7] This approach is further completed by a comparison of XAS with DOS spectra obtained either by theoretical band-structure calculations or by experimental measurements such as BIS in order to distinguish between the DOS and the core-hole effects. At this point the classical core exciton, as treated by the impurity model[13] or the polaron model, has to be considered as the particular case of the more general problem concerning the core-hole effects. Particularly if the excitonic structure falls above the CBM, one must take into account the interaction between discrete and continuum states.[14]

In the present work we propose a critical study of this problem by comparing the Cu L_3 edge not only with the LMTO DOS and photoemission as performed in the usual approach, but also with BIS and optical spectra. We limit ourselves to CuCl, as only in this case is the excitonic structure a well-defined line, in opposition to CuBr and CuI which show only a step.

In Sec. II we outline some important features about the experimental measurements, especially for XAS and BIS. In Sec. III we propose a correspondence between BIS and XAS Cu L_3 spectra in comparison with the partial DOS calculated by the LMTO method. This comparison is further extended to reflection spectra in the vacuum-ultraviolet range. Section IV is devoted to a discussion of the results.

II. EXPERIMENT

Cu L_3 is studied on the SU 72 port of Super ACO at LURE.[15] The double monochromator was equipped with two beryl crystals. The resolution is about 0.4 eV. The measurement of the transmitted photon flux is preferred as compared to the yield technique, in order to minimize surface effects, in particular those due to the presence of Cu^{++}. The incident and transmitted photons are measured successively.

To obtain the transmittance, films of CuCl with a thickness of about 2000 Å are evaporated onto thin collodion sheets. The same type of samples are deposited on molybdenum sheets for BIS and XPS measurements. More details of BIS experiments are given elsewhere.[6]

XPS experiments are performed on the VSW spectrophotometer, ESCA 150, equipped with a monochromator (the diameter of the crystal is 300 mm). For these specific XPS measurements it is calibrated by means of the calibration binding energies of Cu $3p$, Cu L_3 MM, and Cu $2p_{3/2}$, as determined by Anthony and Seah.[16] The reflection spectra are measured on cleaved monocrystals with synchrotron radiation.[5,17]

III. EXPERIMENTAL RESULTS AND ENERGY BANDS

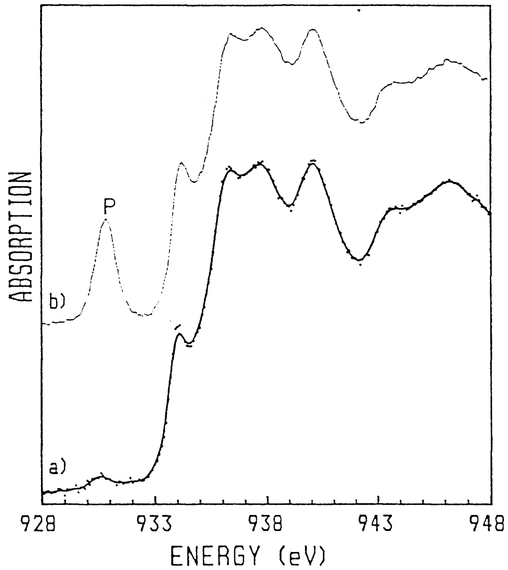

FIG. 1. The Cu L_3 edge in CuCl. In (a) we measure the x-ray photon flux transmitted by the thin layer. In (b) the Cu L_3 is measured in the total yield mode (Ref. 18).

In Fig. 1(a) we display the measured Cu L_3 absorption edge in CuCl. First we point out that the prepeak at 930.7 eV as observed in yield measurements [Fig. 1(b)] (Ref. 18) is very small in our spectra. Since yield measurements are sensitive to the surface properties it is not surprising that they show experimental features related to the presence of Cu^{++}. This means that our spectrum is characteristic of pure bulk CuCl. Here we are essentially concerned with four features: E_X, A_1, A_2, and B [Fig. 2(d)].

To reveal possible excitonic effects and to clarify their nature, the Cu L_3 spectrum is compared with the band-structure scheme. Thus the VBM and CBM in Cu L_3 can be fixed. Two methods can be used. In one the XPS spectrum is studied to measure the VBM-Cu $2p_{3/2}$ separation in order to fix the VBM in the XAS spectrum. To expect a precision of 0.1 eV in the position of the VBM in XAS and also in the evaluation of E_b, a relative error better than 5.10^{-5} eV is required in XPS and XAS measurements. This is not trivial because of the instrumental limitations, and also for physical reasons. In the other method it is essential to have a good understanding of the spectra measured by different spectroscopies and to bring them into correspondence with the help of the band structure. In this way we avoid deep-level and high-energy measurements. In the following the two methods will be extensively studied and discussed.

A. CBM-XPS

In the past only a few works were devoted to core-level measurements by XPS in CuCl. The results are listed in Table I, with the margin of error when available. The VBM-Cu $2p_{3/2}$ separation may be given directly,[19] whereas in Ref. 20 the respective energy positions of Cu $p_{3/2}$ and the nondispersive component (e_g) of Cu $3d$ are reported. We have performed the same measurements, taking special care with the calibration of the electron analyzer with the help of the calibration binding energies as obtained and discussed by Anthony and Seah.[16] These energies concern the Cu $2p_{3/2}$, Cu L_3 MM, and Cu $3p$

lines in Cu measured with Al $K\alpha$ to a precision of 0.020 eV. In this manner we measure the separation of the Cu $2p_{3/2}$ and Cu $3d(e_g)$ in CuCl as 929.31±0.05 eV. To determine the VBM, we look for complementary information. Two-photon absorption,[21] probably the most intrinsic since surface effects are negligible in this type of experiment, gives a value of 1.79 eV for the VBM-Cu $3d$ separation; the error margin may be estimated to be about 0.01 eV. However, this value is obtained at liquid-helium temperature, whereas here we are concerned with room-temperature measurements. Hence the high precision and the intrinsic properties of optical measurements may be partially lost by the thermal shift if this is not known with a good precision. There are no measurements of the thermal shift of e_g with respect to the VBM. We have, nevertheless, obtained an estimate of the thermal shift of valence-band features from the thermal behavior of the valence excitons. The thermal shift of the $Z_{1,2}$ valence exciton is about 2×10^{-4} eV/K when going from 98 to 291 K.[22] However, we may suppose that the shift of Cu $3d$ and Cl $3p$ due to electron-phonon interaction and thermal expansion will not be higher than those of the valence exciton. We have also shown, for CuBr, that dynamical hybridization does not modify the VBM-e_g separation through the mixing rate.[23] From these considerations we see that the indetermination inherent in the use of optical data at 4.2 K with photoemission data at room temperature will not exceed 0.06 eV, the shift of the $Z_{1,2}$ exciton. Thus we obtain the position of the VBM with respect to Cu $2p_{3/2}$, as 931.10±0.11 eV (Table I). It should be also noted that the direct determination of the VBM, which is the beginning of the EDC in our measurements, is 931.51±0.15 eV. However, in this type of measurement we have to deal with possible extrinsic surface effects in addition to instrumental broadening, which is more important when we deal with an edge instead of a peak.

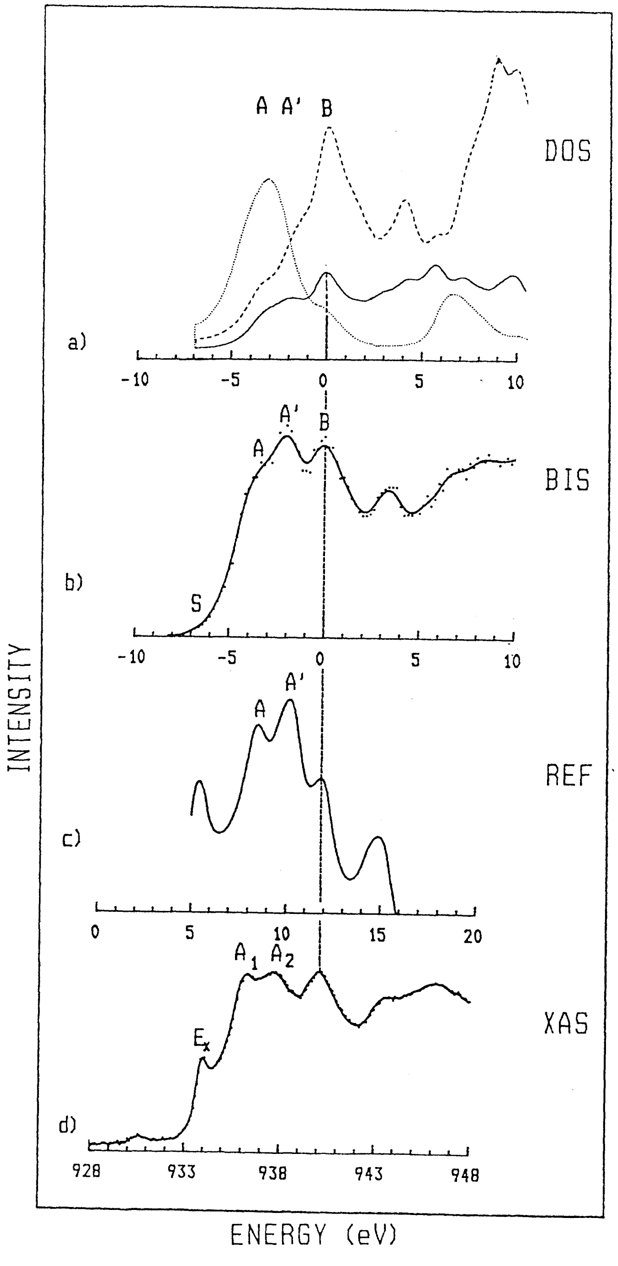

FIG. 2. The structures in the DOS and the BIS are referred to the B peak (Ref. 6). The convoluted partial DOS $(\mathrm{eV})^{-1}$, as given by LMTO in the atomic spheres of copper, are represented: · · · ·, s states; — — —, p states; and ——, d states. The four spectra—DOS, BIS, vacuum ultraviolet reflection (REF), the Cu L_3 (XAS) are shown in correspondence to the B peak.

TABLE I. Valence-band features by XPS measurements with Al $K\alpha$ in eV. In lines 2 and 5 the VBM is located without the intermediate $3d$ Cu(e_g) level. In lines 3 and 4 the VBM-$3d$ Cu(e_g)=1.79 eV±0.07 separation is added to the values of column 2 to obtain the VBM position values (in brackets) given in column 3. In line 3 the precision about the $3d$ Cu(e_g)-$2p_{3/2}$Cu (Ref. 20) is not given; hence the error margin in column 3 is also unknown. In line 5 the error margin is probably higher, as discussed in the text.

	$3d$ Cu(e_g)-$2p_{3/2}$Cu	VBM-$2p_{3/2}$Cu
Goldmann *et al.* (Ref. 19)		931.0±0.1
Van der Laan, Sawatzky, and Haas (Ref. 20)	929.0±*?*	(930.79±*?*)
Present work	929.31±0.05	(931.10±0.11)
Present work		931.51±0.15

Keeping in mind that the main purpose of this study is the position of the CBM in XAS, we look for the thermal behavior of the gap (E_g). It is given as 2×10^{-4} eV/K, so the experimental value of 3.4±0.01 (Ref. 1) at helium temperature should be increased by 0.06 eV in the present study (3.46±0.01 eV). In this manner, including the error in the calibration of the XAS energy scale which is also about 0.1 eV, the CBM is located in the XAS spectrum at 934.56±0.21 eV from Cu $2p_{3/2}$. Finally, the measured position of E_x as 934.10±0.05 eV in the XAS scale gives an E_b energy of 0.46±0.26 eV. Formally, E_x may be attributed to a classical core-hole exciton, as it lies in the forbidden gap. But when the error margin is taken into account this value of E_b is of the same order of magnitude as that of the valence exciton: 0.19±0.01 eV.[1] In any case, in regard to the small value of E_b and a large error margin, it will be useful to investigate how reliable are the high-energy measurements inherent in the present study. The most important uncertainties arise from a comparison of two high energies: the one in XPS measured by comparison with an electrical ramp, the other in XAS measured by comparison with an energy scale given by x-ray diffraction by a monochromator crystal. Here it is essential to note that the final states are not the same in the two spectroscopies.

In XAS measurements the final state is at ~930 eV, whereas in XPS the final state is at 1486.5 eV (Al $K\alpha$) from Cu $2p_{3/2}$. In XAS the excited electron lies in the lower conduction band, whereas in XPS it occupies free-electron states about 500 eV above the CBM. It is quite evident that the Coulomb interaction between the core hole and the conduction electron in XAS will be more important than between the core hole and free electron in XPS. This means that in our case XPS, measured with Al $K\alpha$ photons, probably overestimates the VBM-Cu $2p_{3/2}$ separation with respect to the amount measured in XAS. However, the fact that an extra structure appears in the Cu L_3 XAS [Fig. 2(d)], shows that the core-hole potential obtained through the Coulomb interaction is indeed important. A shift of the conduction band toward lower energy, in addition to the creation of an exciton-like state, is also possible. In view of this possible shift of the core level and the small binding energy of the extra structure as deduced from the comparison of XPS and XAS, the possibility of a core exciton lying in the gap becomes questionable.

B. CBM — band structure, BIS, and optical spectra

Recently, we have shown that when compared with BIS experiments, the LMTO calculations give a realistic picture of the partial density of states (DOS) projected on the Cu site.[6] In Fig. 2(a) we show s, p, and d DOS's on the Cu site convoluted with a Lorentzian with a width at half maximum of 0.6 eV. The energy positions of the triplet structure in BIS [Fig. 2(b)] are well reproduced by the DOS. In Table II these positions are given with respect to the B peak. These calculations confirm that the lowest conduction band is s like, in opposition to Cu_2O, where the lowest band is d like.[24] This is not necessarily reflected by the BIS spectra, because the weight of s orbitals in these spectra are unknown. At the energy corresponding to the B peak, we observe a very intense p DOS (cf. the Cu K white line in XAS) and also a well-defined structure in the d DOS. Hence its energy position will not be affected by the relative weight of the different orbitals. Finally, it is important to note that there is no DOS peak at an energy lower than that of A [Fig. 2(a)].

TABLE II. The energies of the characteristic data for different types of spectra referred to the B peak (in eV). S represents the starting of the BIS curve. In regard to the high noise level, the precision of the BIS data is about ±0.3 eV. For reflection and XAS measurements the error margin is smaller than ±0.05 and ±0.2 eV, respectively.

	S	E_x	A_1	A	A_2	A'	B
DOS				−3.3		−1.8	0
BIS	−6.8			−3.2		−1.8	0
REF				−3.35		−1.74	0
XAS		−6.0	−3.7		−2.4		0

After these comments, we are now able to compare Cu L_3 in XAS with the band-structure features. According to the dipole selection rule, only s and d orbitals of the conduction bands will be involved, the transitions toward d states being more intense ($\Delta l = +1$). In Fig. 2(d) and Table II we present the Cu L_3 spectrum with its three peaks with respect to B. This interpretation of Cu L_3 shows that the E_x structure (−6.0±0.2 eV from B in Table II), lies in an energy range where neither the DOS nor the BIS shows a structure. Hence its origin as a core-hole effect is confirmed. Moreover, it lies in an energy range higher than S [Fig. 2(b)], the beginning of the BIS signal, which means that in this approach it is above the CBM, if the CBM is identified as the start of the BIS signal (−6.8±0.3 eV from B in Table II).

Comparison with the optical spectra may throw some further light on the nature of E_x. In Fig. 2(c) we present the reflection spectrum, measured at room temperature. Formally, it corresponds to the joint density of states (JDOS). It is very surprising to note that in the 10-eV range this spectrum shows quite well the triplet structure as observed in BIS. This means that the initial states in the optical spectra are as narrow as in BIS. In the particular case of CuCl this is quite possible, as the localized e_g is the initial state and the Cu p orbitals are the final states, which also contribute to the shape of the BIS. In this manner B, observed through all the spectra considered here, can be fixed with respect to e_g, which is a well-known datum in the band scheme as we have seen above. In other words the VBM-e_g separation (1.79±0.06 eV), combined with the optical gap CBM-VBM (3.46±0.01 eV), and the position of the B peak in the reflection spectra ($B - e_g = 11.7 \pm 0.1$ eV), gives the B-CBM separation as 6.45±0.17 eV. This value, when compared with that of S (6.8 eV in Table II), suggests that the CBM, within experimental error, is near the start of the BIS signal. Hence the E_x structure at 6.0±0.05 eV from B, lies at 0.45 eV above the CMB with an error margin of ±0.22 eV. This is not in agreement with the conventional picture of a core exciton, which usually should lie in the forbidden gap. Here, to determine the nature of E_x, we have essentially taken into account the correspondence between different types of spectroscopies. The understanding is based only on the physical meaning of characteristic features.

IV. DISCUSSION

The two models developed in Sec. III to evaluate E_b lead to apparently inconsistent results. In one E_x lies below the CBM, with $E_b = 0.46 \pm 0.27$ eV. In the other it should be superimposed on the continuum of the lowest conduction band. This second configuration seems to be more realistic. The XAS and optical spectra, in spite of the fact that they are measured on two different types of samples, are the least sensitive to surface effects like additional lines due to the presence of Cu^{++} complexes.

Hence in the discussion we consider the following: (a) E_x is not a DOS feature. (b) E_x, lying outside the gap, does not represent a conventional core exciton.

When the dipole selection rule for transitions from Cu $2p$ is considered, the $\Delta l = +1$ transition will be about five times higher than $\Delta l = -1$. In this way *d* features will be enhanced as compared to those of *s*. Hence it becomes quite possible that an excitonlike state related to *d* orbitals is more intense than a conventional exciton lying in the gap involving *s* orbitals.

To describe the electronic properties of CuCl, two points are essential. One concerns peculiarities connected to the very localized Cu 3*d* band, and the other is its zinc-blende structure. For the first point we recall some observations made on a copper-based semiconductor (Cu_2O). For the second case it will be worthwhile to consider the Zn L_3 XAS in ZnS, ZnSe, and ZnTe since Zn L_3 falls in the same energy range as Cu L_3, with a comparable hole width. Unfortunately, there are no experiments concerning Zn L_3.[25]

Among copper compounds, Cu L_3 in Cu_2O is probably the most attractive in regard to core excitons, as it was for valence excitons. In an earlier study some structures in this edge were attributed to Wannier exciton series,[26] arguing that the lowest conduction band is *s* like. In a more general study,[27] where Cu_2O is compared to other monovalent or divalent compounds, the main structure at about 2 eV from the Cu L_3 edge is attributed to the 2*p*-3*d* transition. This interpretation is supported by a comparison of the more detailed experimental Cu L_3 with a calculated partial DOS which shows that the contribution of *d* orbitals is the most important at the CBM. Moreover, it is shown that the high intensity and the disymmetry of the main peak result from the broadening of the DOS feature by an excitonic contribution centered typically on the theoretical position of the CBM in the XAS spectrum, and at about 2 eV below the main *d* DOS peak.[24] This excitonic contribution is characterized by a Gaussian with a FWHM of 0.4 eV.

Contrary to Cu_2O, CuCl crystallizes in zinc-blende structure and presents a high degree of ionicity. The partial *s* contribution in the lowest conduction band in CuCl, as calculated by the LMTO method, is more important than that of Cu_2O. In Fig. 3 we give the decomposition of the spectrum assuming an arctan shape to approximate the edge, while the XAS features, for convenience, are fitted by Gaussians. In this decomposition the core and experimental broadenings are taken as 0.55 and 0.4 eV, respectively. It is interesting to note that the best fit with the measured XAS is obtained with a Gaussian where the FWHM is 0.3 eV, to represent the exciton line. This value is comparable to that used in the Cu L_3 edge of Cu_2O. In this decomposition the exciton position lies beyond the inflexion point of the edge (933.36 eV).

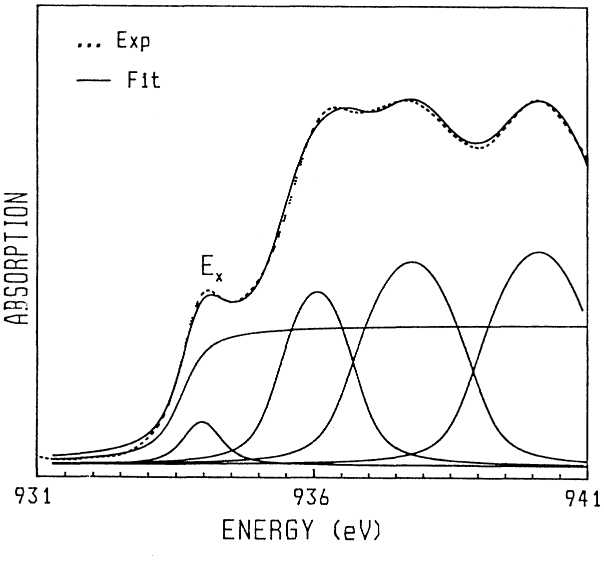

FIG. 3. The decomposition of the XAS takes into account a Gaussian to represent the exciton and a theoretical shape (arctan) to represent the edge. For simplification, A_1, A_2 and *B*, in spite of their DOS nature, are also approximated by Gaussians.

V. CONCLUSION

In this work, to study the core hole in the Cu L_3 edge three points were considered: (1) a comparison between DOS features and excitonic structures, (2) the symmetry of the final state, and (3) the evaluation of the binding energy. The excitonic nature of E_x was clearly established.

The comparison of XPS and XAS measured in the transmittance mode leads to an E_b of 0.46±0.26 eV. This value is of the same order of magnitude as those of valence excitons. Hence the significant contribution of the dynamical screening by the valence excitons, which enhances the E_b of core excitons as compared to that of valence excitons, becomes questionable.

One obtains another conclusion when XAS is compared to BIS and vacuum-ultraviolet spectra. The E_x now lies above the conduction-band minimum. In this configuration the contribution of *d* orbitals as final states becomes considerable. This model presents some analogies with that of Cu_2O, the other monovalent copper compound, although it crystallizes in the simple cubic structure.[24] According to the present study this second situation seems to be more probable, and it is due to the particular behavior of the Cu 3*d* band. However, this should be further verified by other studies, such as comparable XAS experiments on its nearest isoelectronic compound ZnS.

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