Wavelength, energy shape, and structure of the Cu $K\alpha_1$ x-ray emission line

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The shape of the Cu $K\alpha_1$ x-ray emission line was measured with the use of a channeled silicon monolithic double-crystal spectrometer of a novel design. With an accuracy $<1\%$, the only structure detected was a very small shoulder 2.6 eV away from the peak on the low-energy side of it. Values obtained of the full width at half maximum and the index of asymmetry of the line are in good agreement with some of the previously published data. The high stability and accuracy of the spectrometer is demonstrated by the determination of the absolute wavelength of the Cu $K\alpha_1$ x-ray emission line. The result obtained is $\lambda(\mathrm{Cu}\,K\alpha_1) = 1.5405952$ Å (0.85 ppm) on the x-ray scale defined by the National Bureau of Standards value for the lattice spacing of silicon [R. D. Deslattes, E. G. Kessler, W. C. Sauder, and A. Henins, Ann. Phys. (N. Y.) 129, 378 (1980)]. A full discussion of the method is given, and ways of increasing the present accuracy by an order of magnitude are indicated. An analysis of the data within the framework of the many-body theory of photoelectron and x-ray emission spectra is presented. The analysis indicates that while a well-defined value for the lifetime width of the core-hole state can be extracted from the data, this is not the case for the asymmetry parameter. The reasons for this behavior are fully discussed. Finally, a value of 1.73 eV is calculated from the data for the width of the Cu K level.

I. INTRODUCTION

The characteristic x-ray emission lines of the iron-group elements are known to be asymmetric in shape.[1–4] The deviations of these line shapes from the Lorentzian form of higher-Z elements[5] were found to be correlated with the number of unpaired $3d$ electrons[6] thus indicating the crucial influence of these electrons on the line shape. The asymmetries of the lines were, thus, attributed to level splitting due to valence-electron excitation,[7] to Kondo-type many-electron interaction of the conduction electrons with the deep core-hole states,[8] tc electronic interaction in various spin coupling between the complete $3d$ shell and the $2p$ shell which is left incomplete subsequent to the emission of the x-ray photon,[9] and to electrostatic exchange interaction between the $3d$ and the $2p$ shells.[2,10]

For most of the iron-group elements, the experimental evidence concerning fine structure in the $K\alpha_1$ line appears inconsistent.[2,11] A typical example is the Cr $K\alpha_1$ line which was reported in two independent publications to show fine structure.[12] Two subsequent higher resolution and accuracy measurements[11,13] were, however, unable to detect such structures. The Fe $K\alpha_1$ line was reported in two different experiments having comparable resolution and accuracy to be smooth[2] down to an experimental accuracy level of 1% and to show fine structure[14] of $\sim 3\%$ amplitude, respectively. In the Cu $K\alpha_1$ line, the subject of the present research, conventional double-crystal spectrometers were unable to resolve any structure.[2,15] Sauder *et al.*,[16] however, were recently able to detect fine structure by employing a monolithic double-crystal spectrometer. Their device employed basically the (111) reflection of Si in the fourth order rather than the third order used by Tsutsumi *et al.*[2] and, very recently, by Heinonen *et al.*[15] This, in addition to the inherently higher stability of their monolithic device, resulted in a higher energy resolution.

Clearly, more high-resolution data would be desirable before final conclusions can be drawn in confidence as to which, if any, of the proposed theoretical mechanisms actually takes part in the x-ray emission process and what are their relative importance.

We have therefore undertaken to remeasure the line shape of the Cu $K\alpha_1$ line, with high accuracy and resolution, with the use of a channeled monolithic double-crystal spectrometer of a novel design. The results obtained indicate a very small and rather wide shoulder on the low-energy side of the peak at a distance of 2.6 eV from it. Excluding this feature, discernible also in the data of Sauder

et al.[16] and Heinonen *et al.*,[15] no structure was detected in the line shape to within our 1% accuracy. Values of the full width at half maximum (FWHM) of the line and its index of asymmetry, as calculated from our data, agree well with previously published values.

The data is also discussed within the framework of the many-body theory of x-ray emission. Originally, this theory had been proposed by Mahan[17] and Nozières and de Dominicis[18] to account for x-ray effects observed near absorption edges in metals. It was later extended by Doniach and Šunjić[8] (DS) to account for the asymmetric shape of both the x-ray excited electron photoemission (XPS) and the characteristic x-ray emission (XES) lines of metals. The DS theory was extensively and successfully applied to XPS line shapes observed in metals[19–21] and metallic compounds.[22] In contrast, only very few studies[20,15] were undertaken to test its validity for the characteristic x-ray emission line shapes measured in practice. Cu, being a member of the iron-group elements (where large asymmetries of the line shape have been observed[1–4]), is a natural testing ground for this theory. Our analysis yields a well-defined value for the core-hole-state lifetime width, but a rather poorly defined one for the asymmetry parameter. This problem is shown to arise from the details of the line shape and its resolution must await further theoretical development.

II. EXPERIMENTAL

A. The general method

The energy dispersive device employed was a monolithic double-crystal x-ray spectrometer (MDCS).[16] This is, in effect, a single perfect crystal where two sets of Bragg planes play the role of the two separate crystals of a conventional double-crystal spectrometer (DCS).[23] The angle β_0 between the two "crystals" of the MDCS is therefore fixed. Nevertheless, a limited range of energy tuning can be obtained by relaxing the requirement of coplanarity of the wave vector of the incoming beam and the normals to the two Bragg planes. In practice this is done by tilting one or both Bragg planes relative to the horizontal plane of dispersion.[24] We chose to rotate our device about the normal to the first Bragg plane. The situation is mathematically identical with that of a conventional DCS with the second crystal tilted relative to the plane of dispersion. If the axis of rotation is perfectly perpendicular to the first set of Bragg planes then the wavelength λ transmitted by the MDCS is given by[25,26]

$$\lambda = 2d_1 \sin\beta \cos\delta_2 / [(d_1/d_2 + \cos\beta\cos\delta_2)^2 + \sin^2\beta\cos^2\delta_2]^{1/2} , \quad (1)$$

where d_1 and d_2 are the spacings of the first and second sets of planes, respectively. δ_2 is the angle between the normal to the second Bragg plane and the plane of dispersion, and β is the projection of the angle β_0 between the two sets of planes, on the plane of dispersion. Both β and δ_2 are functions of the angle of rotation α:

$$\sin\delta_2 = \sin\alpha \sin\beta_0 ,$$
$$\tan\beta = \cos\alpha \tan\beta_0 . \quad (2)$$

The MDCS has several advantages over the DCS for this type of measurement. Since it is monolithic, it has higher inherent stability than the DCS. It requires fewer adjustments, since its "crystals" are already aligned one relative to the other. In fact, the only adjustment required is that of aligning the axis of rotation perpendicular to the first Bragg plane, which can easily be done to high accuracy.[27] Since Eq. (1) is even in α, a complete scan in α will produce, for a single emission line, a spectrum containing two peaks: one for $+\alpha_p$ and one for $-\alpha_p$, where $|\alpha_p|$ corresponds through Eq. (1) to the wavelength of the emission line. The midpoint between the two peaks, which corresponds to $\alpha=0$, can therefore be determined to high accuracy and the zero-point error[26] is thus eliminated. If the two sets of planes can be so chosen that only small rotations α are required for scanning, an additional advantage emerges. Owing to the high perfection of the crystal, the interplanar angle β_0 is known to high accuracy, and therefore the error in the relatively small α will contribute only very little to the total relative error in the effective angle between the two "crystals" of the spectrometer. Moreover, it is well known[28] that the Bragg angle of a tilted set of crystal planes changes with the square of the angle of the tilt. Thus, a change in the transmitted wavelength, which is affected by a small change in the effective Bragg angle at the second set of planes of the MDCS, will require a rotation α much larger than that required in the conventional DCS for the same change in the transmitted wavelength. In the device used by us, for example, the full width at half maximum of the Cu $K\alpha_1$ line corresponds to a rotation of $\sim 40'$ of arc, while for a DCS the rota-

tion required only a few tens of seconds of arc. Therefore the requirements on the accuracy of measurement of the angle of rotation can be relaxed by a factor of up to 100 in this case. This point is an especially advantageous feature when measurements of very small line shifts due to chemical, thermal, or any other effects are conducted. The large rotation in α required for even small wavelength shifts will allow high accuracy in the angle measurements, and hence in the line shifts.

B. Detailed x-ray optical design

The actual device used for the measurements was designed to employ two symmetrical reflections in each set of Bragg planes. This was achieved by cutting a channel parallel to each set of planes as shown in Fig. 1. A conventional DCS of similar design was recently proposed by Hrdý[29] while Sauder *et al.*[16] used the corresponding single reflection MDCS. The advantages of our design are threefold: First, the shape of the resolution function is improved by almost completely eliminating contributions to the intensity from the wings of the single-crystal reflection curve. Second, the geometry of the device greatly reduces the background scattered thermally or otherwise by air, the surfaces of the crystal, etc., into the detector. Finally, it very much reduces the chances that spurious simultaneous Bragg reflections from other planes will reach the detector. This last point is very important since while the first two contributions are slowly varying or constant as the device is rotated, simultaneous reflections produce narrow peaks. These, superimposed on the line profile, could easily be misinterpreted as fine structure.

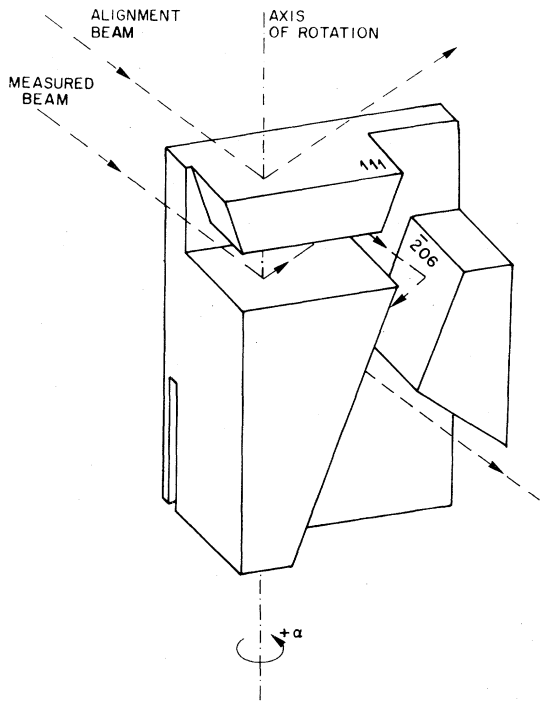

FIG. 1. Channeled monolithic double-crystal spectrometer. Note the strain isolation spring at the back and the upper surface, which is used for *in situ* alignment of the device.

A very effective method of identifying such spurious structure is the comparison of data measured by scanning clockwise ($\alpha < 0$) and counterclockwise ($\alpha > 0$). If the axis of the zone to which the two Bragg planes belong does not have a structural mirror plane perpendicular to it, a spurious reflection will appear as structure on one of the peaks only. Thus, any structure not detected in both peaks is necessarily caused by the crystal and is not a spectral feature.

The MDCS was fabricated from a single dislocation-free silicon crystal[30] block of dimensions $28 \times 30 \times 16$ mm^3. The planes employed are (333) and ($\bar{2}06$) as the first and second sets of Bragg planes, respectively, and the Cu $K\alpha_1$ peak is obtained, therefore, at $|\alpha_p| = 3.68°$. These planes were chosen in order to avoid any mirror plane so that spurious structure in the line-shape data can readily be identified. The energy resolution of the MDCS is basically determined by the width of the narrowest of the two reflection curves employed. In our case it did not exceed a few hundredths of an eV. The device incorporates a strain-isolation spring cut at its back to ensure that the actual interplanar angle does not deviate from the theoretically calculated one due to mounting strains. A brass stud epoxied to the lower end of the spring was used to mount the crystal on a simple two-axis alignment device whereby the (111) plane was aligned[27] perpendicular to the axis of rotation using the (333) reflection from the upper surface of the crystal. The alignment device was in turn mounted on a precision rotary table equipped with a geared step motor drive. The source employed was a commercial sealed x-ray tube operated on a dc current and voltage stabilized Enraf generator. The data were collected stepwise under computer control[31] and are the sum of many short scans through both the positive and the negative α peaks, each consisting of a few hundred data points. This

way fluctuations in the source intensity were averaged out.

III. DISCUSSION OF RESULTS

A. Absolute wavelength of the Cu $K\alpha_1$ line

A typical set of data is given in Fig. 2. The angular positions of the peaks of the two line shapes were determined from the data by the well-established method[26,32] of fitting the upper half of each peak by a six-degree polynomial using the least-squares method, and calculating the peak position from the polynomial. The peak wavelength of the Cu $K\alpha_1$ line is the value of λ corresponding, through Eq. (1), to half the angular distance between the peaks. The values of d_1 and d_2 in Eq. (1) were calculated with the use of a unit-cell edge[33–35] $a_0 = 5.431\,028$ (22.5 °C). This is accurate to < 100 parts per 10^9 (Ref. 36). Correction for refraction[37] was also applied. The peak wavelength value λ_p obtained was then corrected for the vertical divergence of the beam,[26] which amounted to a decrease of 0.57 ppm in λ_p. The residual tilt of the axis of rotation relative to the [111] direction was measured[27] several times during the experiment and was found to be stable at a value of 45″ of arc. This called for a further decrease of 0.40 ppm in λ_p.

The largest contribution to the uncertainty in the value of λ_p thus obtained is that of the error in locating the exact angular positions of the peaks.

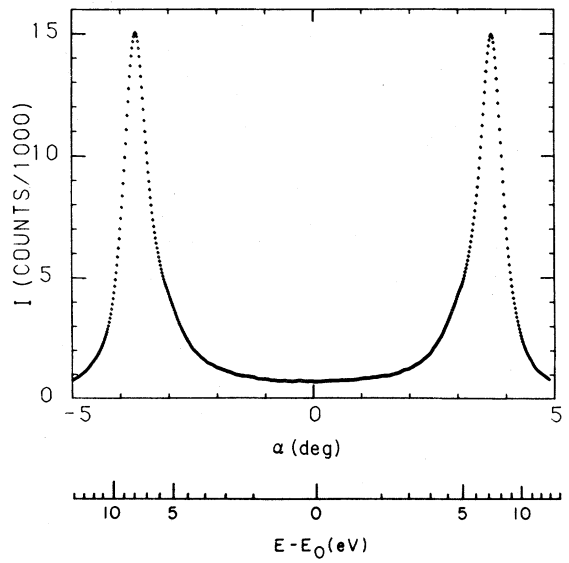

FIG. 2. Complete spectrum of the Cu $K\alpha_1$ emission line taken with the device in Fig. 1.

The error is given by[38]

$$\sigma_p = W 1.52/(N_p n)^{1/2} ,$$

where σ_p is the standard deviation of the position of the peak, W is the angular FWHM of the peak, N_p the number of counts at the peak, and n is the number of points used in fitting the six-degree polynomial to the data. In our case, $N_p = 15\,500$, $n = 40$, and $W = 0.6397°$ so that $\sigma_p = 0.001\,23°$. Through Eq. (1) this corresponds to an uncertainty of 0.62 ppm in λ_p. An additional uncertainty of 2″ of arc in the measurement of the angle of rotation contributes 0.28 ppm to the error budget. Since periodic temperature changes with periods larger than a single scan (which was the actual case) tend to broaden the peaks a little but do not influence their position, effective temperature variations were estimated to be ± 0.2 °C which, with a linear coefficient of expansion of 2.56×10^{-6} per °C for Si,[39] adds an uncertainty of 0.51 ppm in λ_p. These uncertainties have to be added quadratically, and we finally obtain

$$\lambda(\text{Cu } K\alpha_1) = 1.540\,595\,2 \pm 0.000\,001\,3$$

in units of Å. This corresponds to an accuracy of 0.85 ppm. These values agree with those obtained by Deslattes and co-workers[33,34] to within the combined accuracy of the two experiments.

The error-budget analysis given above indicates how these measurements can be improved. Temperature stabilization to 0.02 °C and angle measurements to 0.2″ of arc, both not too difficult to achieve in practice, will reduce the respective errors to below 0.05 ppm. Employing a rotating anode x-ray generator instead of the low-power sealed x-ray tube used by us will result in a 20-fold increase in the accuracy in peak location. This corresponds to an error of 0.03 ppm in wavelength. Measurement statistics can be further improved by the use of a stationary, nonrotating MDCS and a beam that diverges in the plane of dispersion. Detection by a horizontal linear position-sensitive detector will enable the simultaneous collection of a complete spectrum instead of one point at a time. Axis misalignment can be made negligible by employing double-crystal-alignment methods. Thus, the total uncertainty in wavelength measurements with the use of our type of MDCS can be held to 0.08 ppm without excessive difficulty.

We have thus demonstrated the high accuracy and ease of construction, alignment, and operation of the channeled monolithic double-crystal spectrometer. These qualities as well as its ruggedness, inherent stability, and very low cost render it a

highly competitive and, in many cases, a superior alternative to conventional double-crystal spectrometers.

B. The Cu $K\alpha_1$ line shape

In spite of the high resolution and good statistics, no evidence of fine structure is observed in the data, Fig. 2. A special method for the identification of small consistent trends buried in the statistical noise of measured data was developed and applied to the spectrum of Fig. 2. The method consists of numerical calculation of the first and second derivatives of the data.[40] A repeated three-point binomial moving average smoothing[41] is employed in order to suppress spurious oscillations. Various techniques are used to ensure that no oversmoothing of the data and the derivatives occurs. Figures 3(a) and 3(b) give the first and second derivatives of the data of Fig. 2. An examination of Fig. 3(b) reveals several minima which indicate possible structure in the data of Fig. 2. As mentioned above, however, only features common to both peaks must be considered valid structure. Thus, all minima in Fig. 3(a) except the one at $E \approx 4.8$ eV are ruled out. This minimum corresponds to a very small shoulder which can barely be detected in Fig. 2 on the low-energy side of the Cu $K\alpha_1$ peak. The position of the shoulder is defined as the E coordinate of the corresponding minimum in the second derivative. This was found to correlate linearly with the number of combined smoothing cycles applied to the data and the first derivative, with a correlation coefficient greater than or equal to 0.995. Extrapolation to zero smoothing cycles gives a separation of 2.6 eV between the positions of the Cu $K\alpha_1$ peak and the shoulder. The same shoulder is discernible in the data of Sauder *et al.*[16] as well as in the recent data of Heinonen *et al.*[15] Note that no other structure was detected and, in particular, no shoulder or peaks were found on the high-energy side of the line. The possibility that the above-mentioned small temperature variations may have smoothed out possible structure in our data was explored by computer simulations. The results indicate however, that only structures less than $\frac{1}{2}\sigma$ of the data would be washed out. Thus temperature variation will leave any features that are larger than the statistical error level of our data clearly discernible.

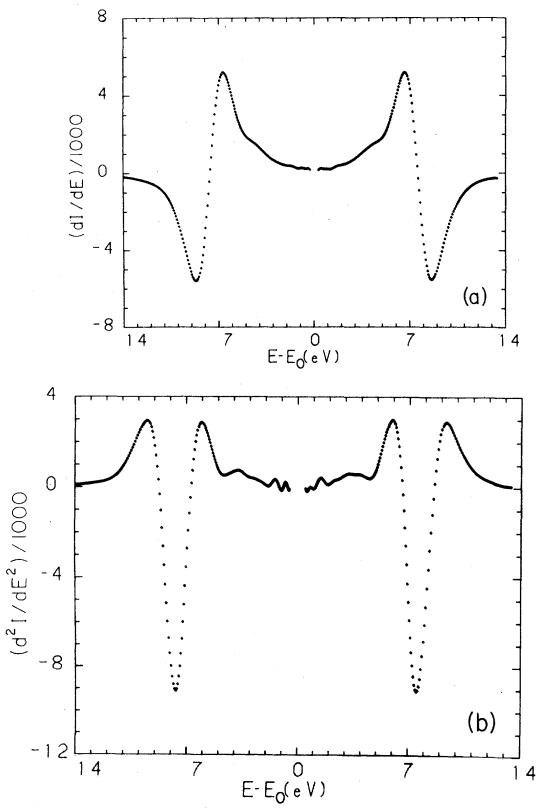

FIG. 3. Complete spectrum of the Cu $K\alpha_1$ line. $E_0 = 8040.271$ eV and corresponds through Eq. (1) to a rotation $\alpha = 0$. Step size in α was 1′ of arc. (a) First derivative of the data. (b) Second derivative of the data. Note the minima at ~4.8 eV corresponding to the shoulder in Fig. 2.

The double-vacancy theory[16] predicts the center of gravity of the multiplet structure to lie at the low-energy side of the peak,[42] in the vicinity of a closely spaced group of multiplet lines ~2.5 eV away from the peak. These two features may perhaps be responsible for the shoulder mentioned above. The theory also predicts the most intense single multiplet line to lie rather close to, and on the high-energy side of the peak (see Fig. 1B in Ref. 16). The fact that this feature was not detected in our experiment may be attributed to the finite resolution of our MDCS as well as to the increased absolute statistical errors in the regions straddling the peak. While on general grounds double-vacancy effects more than likely play an important role in the x-ray emission process of Cu $K\alpha_1$ (as they were recently shown to do in the Cu $K\beta_{1,3}$ line[43]), their unequivocal manifestation as structure is absent from our data. We have therefore to conclude that no decisive evidence in favor of the double-vacancy theory can be obtained from our data.

The data cannot be interpreted in terms of the exchange-interaction theory of Tsutsumi[2,10] either,

although the data shows qualitatively the two-component line structure predicted by this theory for the iron-group elements.[44] Application of the theory to our data would require the existence of $3d$ holes in solid copper. As pointed out by Heinonen *et al.*[15] this is highly unlikely, as indicated by the absence of the corresponding strong satellites in the electron photoemission spectrum of copper.[45,46] In any case, the separation of the shoulder from the main peak is much larger than predicted by Tsutsumi's theory for any of the iron-group elements.

The shoulder could possibly be attributed to shake-up effects of the type suggested by Bloch[47] and Åberg and Utriainen,[48] where an electron is ejected simultaneously with the emission of the x-ray photon. A comparison of the 2.6-eV gap between the positions of the shoulder and the $K\alpha_1$ peak with the values of 2.1, 2.7 (Ref. 49), and 2.3 eV (Ref. 50), calculated with the use of different methods for the gap between the top of the $3d$ band and the Fermi level in Cu suggests that in our case a $3d$ electron is raised above the Fermi level, rather than ejected, while the x-ray photon is emitted. However, in the absence of calculated values for the relevant matrix elements, this interpretation should be regarded at present as tentative only.

Results of a scan of the slope region of the $\alpha < 0$ peak are given in Fig. 4. This scan was done with half the stepsize of the one of Fig. 1, and twice the number of counts per point were collected. As Fig. 4(b) indicates, no high-frequency structure is found in the data; the difference between the original and the well-smoothed data is less than the 2σ level of the data everywhere. The shoulder appears clearly in the calculated second derivative. The changes of the second derivative at the ends of the data interval are artifacts introduced by the numerical procedures. The results given in Figs. 2 and 4 were measured with a load of 35 kV @ 16 mA on the tube. Data was also collected with 20, 25, and

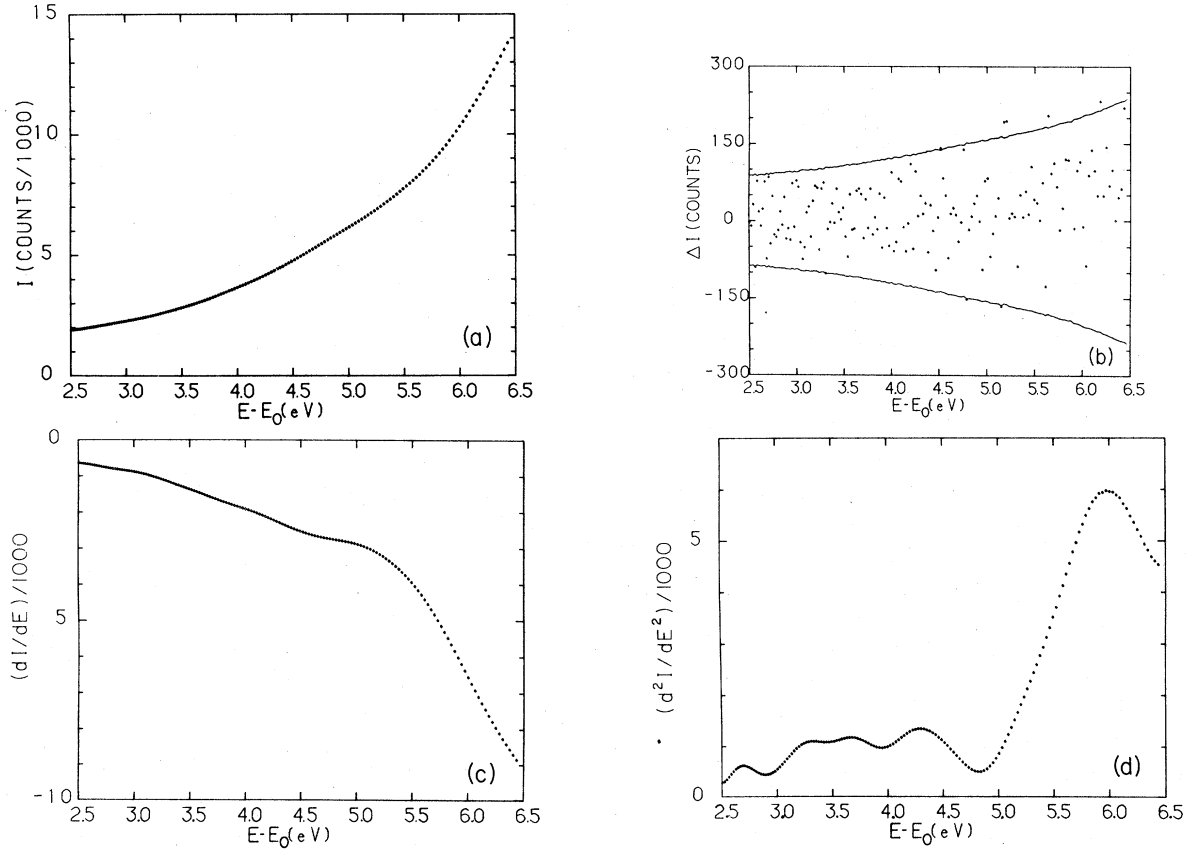

FIG. 4. High-resolution scan of the low-energy slope region of the left-hand peak in Fig. 2. Step size in α was 30″ of arc. (a) Data obtained from the scan. (b) Difference between raw and well-smoothed data (points). Lines indicate the 2σ level of the data. Note that except for very few, all points are well within the 2σ limits, thus indicating that no high-frequency structure is present in the data. (c) First derivative of the data. (d) Second derivative of the data. Note the minimum at 4.8 eV which corresponds to the shoulder in Fig. 2.

TABLE I. Full width at half maximum and index of asymmetry of the Cu $K\alpha_1$ x-ray emission line.

Source	FWHM (eV)	Index of asymmetry
Experimental		
Lee and Salem[a]	2.56±0.19	1.12±0.11
Citrin *et al.*[b]	2.39±0.10	
Tsutsumi and Nakamori[c]	2.84	1.10
Blokhin[d]	2.76	1.2
Meisel and Nefedow[e]	2.48	1.02
Parratt[f]	2.40	1.15
Obert and Bearden[g]	2.38	1.15
Heinonen, Leiro, and Suoninen[h]	2.30±0.05	1.06±0.02
Heinonen, Leiro, and Suoninen[i]	2.42	
Present work	2.61±0.05	1.11±0.03
Theoretical		
Citrin *et al.*[b]	2.21	
Citrin *et al.*[j]	2.08	
Krause and Oliver[k]	2.11	

[a]Reference 4.
[b]Reference 3.
[c]Reference 2.
[d]M. A. Blokhin, *The Physics of X-rays*, 2nd ed., Report No. AEC-tr-4502 (USAEC, Washington, D.C., 1961).
[e]A. Meisel and W. Nefedow, Z. Chem. 1, 337 (1961).
[f]L. G. Parratt, Phys. Rev. 50, 1 (1936).
[g]L. Obert and J. D. Bearden, Phys. Rev. 54, 1000 (1938).
[h]Reference 15 with background subtraction.
[i]Reference 15 without background subtraction.
[j]See note d in Table II in Ref. 3.
[k]Reference 52.

45 kV. Within the accuracy of this experiment, no changes in the shape and position of the peaks occurred upon changing the tube voltage.

The exact positions of the peaks were determined by fitting the upper half of each peak by a six-degree polynomial using the least-squares method and using this polynomial to calculate the positions, the FWHM and the indices of asymmetry of the peaks.[26,32] Results calculated in this way from our data are given in Table I, where previously published values are also listed. The agreement between the more recently measured linewidth data and ours is very good although there are some deviations from the older data. However, in view of the absence of error estimates and the probable over correction for instrumental distortion in the older data,[51] it is doubtful that these differences have any significance. Both the linewidth and the index of asymmetry of Heinonen *et al.*,[15] which were published after the completion of our work, seem to deviate slightly from our values. This may be a real effect caused by the different methods of excitation, fluorescence excitation in their case and direct electron bombardment in ours. Alternatively it may be an artifact of the data analysis caused by the exceptionally high background in the data of Heinonen *et al.*[15] $\gtrsim 3\%$ of the peak height, while in ours it is an order of magnitude smaller. As our experience indicates, the values obtained for both the linewidth and the index of asymmetry are very sensitive to background subtraction. The theoretical linewidths are consistently lower than the experimental ones. This reflects the extreme difficulty in taking into account properly a host of effects which tend to broaden the line.[52,7] As for the index of asymmetry, there is very good agreement between all published data, except that of Meisel and Nefedow. The reason for the deviation of this single value from all other measurement is not known.

C. Many-body effects in the line shape

The theory of Doniach and Šunjić[8] (DS) states that the x-ray line shape is distorted by the many-pair excited state in which the Fermi sea is left

subsequent to the emission of an x ray. The shape is further modified by the finite lifetime of the core-hole state. The resulting line-shape function is given by[8]

$$Y(E)\sim\Gamma(1-\beta)\cos\{\pi\beta/2+(1-\beta)\tan^{-1}[(E-E_0)/\gamma]\}/[(E-E_0)^2+\gamma^2]^{(1-\beta)/2}\,, \tag{3}$$

where Γ denotes the usual gamma function, E_0 is the zero of the energy scale, which in this case does not correspond to the maximum of the line shape, γ is the lifetime width of the core-hole state, and β is the asymmetry parameter of the line. Equation (3) is thus characterized by an index of asymmetry β and a width parameter γ, and has qualitatively the right form: a Lorentzian with a tail on its low-energy side. The parameters β and γ can both be determined by fitting Eq. (3) to the experimentally derived line shape.

The situation is more complicated where the measured line shape incorporates additional structure. In our Cu $K\alpha_1$ data a small shoulder was detected at a distance of $\sim$2.6 eV from the peak on its low-energy side. The recently published data of Heinonen *et al.*,[15] as well as the data of Sauder *et al.*,[16] reveal the same structure (see Fig. 1 in Ref. 15 and Fig. 1 in Ref. 16). As discussed earlier, the origin of this feature is theoretically unclear as yet. One should therefore be very careful in fitting Eq. (3) to such data. The influence of the shoulder on the fit must be neutralized. This was done in our case in four different ways:

(a) Excluding the interval [8043.5, 8046.7] straddling the shoulder, from the fit.

(b) Fitting the data by two skewed Lorentzians[32] having the same widths and indices of asymmetry but different positions and heights. This follows the procedure of Tsutsumi and Nakamori.[2] This resulted in the large Lorentzian being centered on the peak and the small one about the shoulder. The small Lorentzian was then subtracted from the data, and the new set was fitted by the DS profile.

(c) Same as (b) but with two DS profiles (instead of skewed Lorentzians) having the same β and γ but different positions and heights.

(d) Same as (c) but with β and γ unrestricted.

A fit of the single DS profile to the full set of raw data was also performed. The fitting procedure[53] employed the nonlinear least-squares method and the variance matrix was checked to ensure meaningful results. The results obtained for β, γ, and the mean standard deviation σ of the data from Eq. (3) for both the R and the L peaks are listed in Table II, together with values obtained for a single DS profile and the raw data. Figures 5 and 6 give graphic representations of the fits obtained for case (b) above and for the raw data, respectively. As Fig. 6 and the values of σ in Table II show, Eq. (3) does not fit the raw data very well, and the values of β and γ obtained are too high. Table II also indicates that while all the procedures yield the same value for γ to within $\sim$2%, values of β span a range of 300%. This demonstrates the extreme sensitivity of β to even small changes in the low-energy tail of the peaks, as is to be expected. We also noted that values of γ and β obtained from the fit are quite sensitive to the value assigned to E_0. We had therefore included E_0 in the list of parameters and fitted the complete profile to the data, thus determining β, γ, E_0, and the peak height simultaneously. The procedure recommended by Citrin *et al.*[20] of obtaining γ by fitting the high-energy side first and then β by fitting the low-energy side with the use of the value of γ obtained previously may lead, in our opinion, to inaccurate values of β and γ due to an incorrectly chosen E_0.

Thus from Table II we conclude that for Cu $K\alpha_1$,

$$\gamma=1.216\pm0.009$$

TABLE II. Parameter values obtained from the fit of the DS theory to the data. L and R denote the two peaks obtained in a single scan. For the different procedures, see text.

	L			R		
Procedure	β	γ	σ	β	γ	σ
Raw data	0.0489	1.276	188.3	0.0532	1.258	197.2
(a)	0.0296	1.227	81.5	0.0387	1.221	72.3
(b)	0.0093	1.223	80.1	0.0117	1.214	86.2
(c)	0.0140	1.219	69.9	0.0218	1.215	68.7
(d)	0.0136	1.210	71.5	0.0160	1.197	92.7

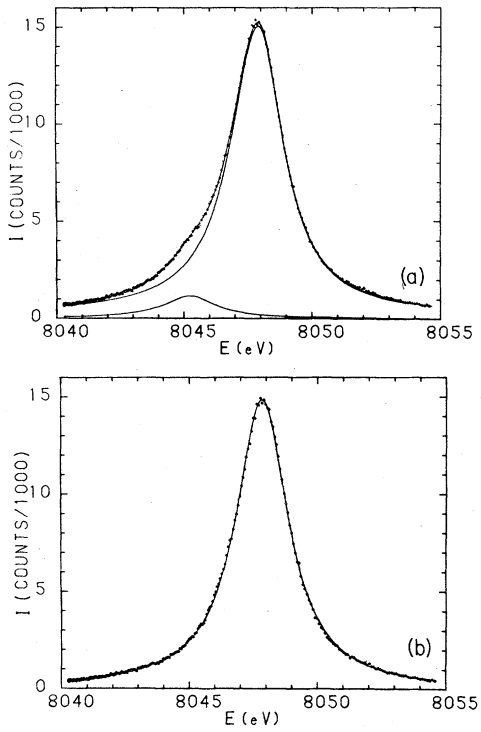

FIG. 5. Fitting a DS profile to the data, using procedure (b) in the text. (a) Fitting the two skewed Lorentzians (continuous lines) to the raw data (denoted by points). The sum of the two Lorentzians, passing through the experimental points is also depicted. (b) Fitting of the DS profile, after subtracting the smaller skewed Lorentzian from the raw data. Note the absence of the shoulder appearing in (a).

(in units of eV), where the value above is the mean of those of Table II and the error corresponds to $\pm 1\sigma$. This lifetime width, in conjunction with the 0.7-eV width of the Cu L_{III} level[46] (for which no estimated uncertainty is quoted), yields a width of 1.73 eV for the Cu K level, in satisfactory agreement with the recent value of 1.55 ± 0.08 eV of Krause and Oliver.[52] As for the asymmetry parameter, no well-defined value can be extracted from the data until theory will enable us to properly account for the shape and position of the extra structure detected in the line shape. All we can say now is that the data indicates that many electron effects of the type predicted by the DS theory indeed cause some distortion in the line shape of the Cu $K\alpha_1$ emission line. A realistic assessment of magnitude of this effect, however, will have to await further theoretical developments.

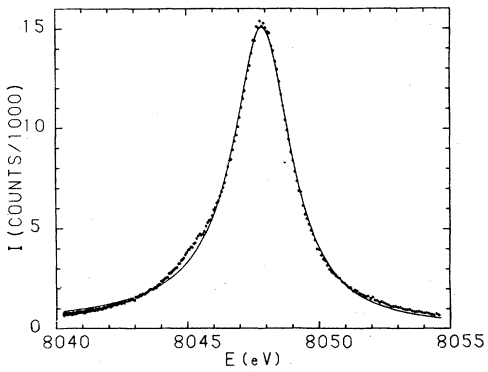

FIG. 6. Best fit of a single DS profile to the raw data.

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