# Structure and wavelength of the Cu $K\alpha_2$ x-ray emission line

Nissan Maskil and Moshe Deutsch
*Physics Department, Bar-Ilan University, Ramat-Gan, Israel*
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The Cu $K\alpha$ emission spectrum was measured with a novel channeled monolithic double-crystal spectrometer. The wavelength of the Cu $K\alpha_2$ line was determined to be $\lambda(\text{Cu } K\alpha_2)=1.544\,425\,6$ Å (1.2 ppm). A small shoulder was detected on the low-energy side of the $K\alpha_2$ peak at a shift of 2.2 eV. To an accuracy lower than 1%, no other structure was detected. The width and asymmetry parameters obtained for the $K\alpha_2$ peak are in good agreement with previous measurements. The $K\alpha_2$ line shape is analyzed within the framework of the radiative-Auger and many-body-excitation theories of x-ray emission. A well-defined lifetime width of the $K\alpha_2$ line is obtained, yielding a $K$-level width of $1.56\pm0.04$ eV, in excellent agreement with theoretical and semiempirical predictions. The applicability of the radiative-Auger, multivacancy, and many-body theories to the measured data is discussed.

## I. INTRODUCTION

The deviation of the characteristic x-ray emission lines of the iron-group transition metals[1,2] from the symmetric shape observed in higher-$z$ metals[3] is universally attributed to multielectronic effects. The specific nature of these effects and their relative importance remains, however, a controversial issue. Level splitting due to excitation of valence electrons,[4] Kondo-type many-electron interaction of conduction-band electrons with the inner-hole states,[5] and various types of incomplete $3d$-$2p$ shell interactions[2,6] have been suggested.

The x-ray spectroscopic evidence for fine structure in the emission lines of the iron-group elements seems mostly inconsistent.[2,7] For copper, the subject of the present study, three conventional double-crystal-spectrometer (DCS) studies revealed no fine structure in the $K\alpha_{1,2}$ doublet.[2,8,9] Sauder *et al.*,[10] using their novel single-reflection monolithic double-crystal spectrometer (MDCS), detected some fine structure in the doublet, most of it in the $K\alpha_2$ line. Deutsch and Hart[11] subsequently studied the $K\alpha_1$ line using a channeled MDCS, and were unable to resolve any fine structure, except for a small and wide shoulder approximately 2.6 eV downshifted from the peak, which was also observed in all previous studies. The Cu $K\alpha_2$ line was, however, out of the range of the MDCS used.

A new MDCS designed for studying the Cu $K\alpha_2$ line with high resolution and accuracy was constructed. The results obtained using this device are presented here. They indicate a very small shoulder on the low-energy side of the $K\alpha_2$ line, approximately 2.2 eV from the peak. No other structure was resolved in the line shape to within the $\lesssim 1\%$ accuracy of the experiment. The index of asymmetry, full width at half maximum (FWHM), and the $K\alpha_2$-to-$K\alpha_1$ intensity ratios agree well with previous measurements.

The $K\alpha_2$ line shape was analyzed within the framework of the many-body theory of x-ray emission of Doniach and Sunjic[5] (DS). As was the case for the $K\alpha_1$ line,[11] a well-defined core-hole lifetime in good agreement with theory is obtained, but no well-defined asymmetry parameter can be derived from the data.

## II. EXPERIMENTAL

The MDCS has been fully discussed elsewhere[10–12] and only a brief description will be given here. The MDCS employs two sets of Bragg planes of the same crystal block to play the roles of the two separate crystals of a conventional DCS. To enhance the resolution, two consecutive reflections in a channel cut parallel to each set of planes are employed. Wavelength tuning is done by rotating the monolith at an angle $\alpha$ about axis perpendicular to the first set of reflecting planes. This results in a tilt of the second set of planes relative to the plane of dispersion, thus changing its effective Bragg angle. The wavelength transmitted by the MDCS is given by[11–13]

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

where $d_1$ and $d_2$ are the spacings of the first and second sets of planes, and $\delta_2$ and $\beta$ are given by

$$\begin{aligned}&\sin\delta_2=\sin\alpha\sin\beta_0\ ,\\ &\tan\beta=\cos\alpha\tan\beta_0\ .\end{aligned} \tag{2}$$

Here $\alpha$ is the rotation angle and $\beta_0$ is the angle between the two sets of planes. The compact, monolithic design eliminates many of the adjustments required in conventional DCS, as its "crystals" are already aligned one relative to the other. It also renders the device highly stable and immune to temperature variations, vibrations, etc. Finally, as Eq. (1) is an even function of $\alpha$, a single emission line will produce two peaks, one at, say, $+\alpha_P$, and the other at $-\alpha_P$, thus allowing $\alpha=0$ determination to high accuracy and also identifying spurious spectral features as those not appearing in both peaks.

 

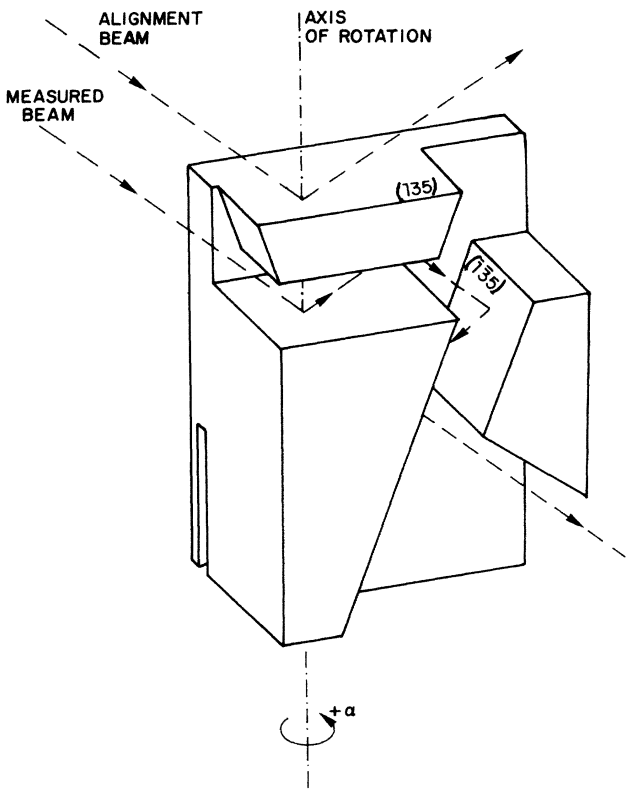


FIG. 1. Channeled monolithic double-crystal spectrometer (MDCS). The upper surface and beam are used to align the axis of rotation perpendicular to the (135) planes.

The monolithic spectrometer used in this experiment, of dimensions $45\times37\times29$ mm$^3$, is shown in Fig. 1. It employs two reflections in channels cut parallel to the (135) and ($\bar{1}35$) planes. For these planes, Eq. (1) yields $|\alpha_P| = 12.69°$ for the Cu $K\alpha_1$ line. The energy resolution of the MDCS is basically determined by the widths of the reflection curves and is of order $10^{-2}$ eV for the planes used here. The MDCS was mounted on a specially constructed computer-controlled goniometer having two perpendicular axes, one for adjusting the angle of incidence $\theta$ on the first Bragg plane and the other for scanning $\alpha$. The radiation source was a commercial sealed x-ray tube run at 30 kV and 16 mA off a stabilized constant-potential Picker generator. As in the previous study,[11] no changes were noticeable in the spectrum when varying the voltage from 25 to 45 kV.

## III. RESULTS AND DISCUSSION

### A. Absolute wavelength of the Cu $K\alpha_2$ line

A typical measured spectrum is shown in Fig. 2. The angles $\alpha_1$ and $\alpha_2$ of the peaks of the $K\alpha_1$ and $K\alpha_2$ lines were determined[13] by least-squares fitting a six-degree polynomial to the upper half of each line and calculating the peak positions from that polynomial. Recent measurements revealed a 1.8-ppm ambiguity[14,15] in the exact value of the lattice spacing of silicon, as well as a possible 0.2-ppm level distortion[16] of the unit cell. The ambiguity

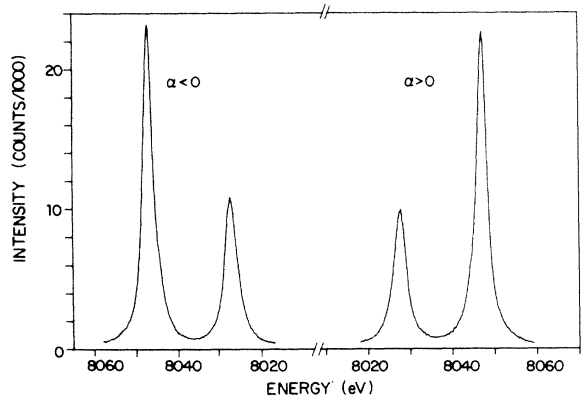


FIG. 2. Complete Cu $K\alpha$ x-ray emission spectrum obtained by rotating the MDCS from $\alpha\approx-13°$ to $\alpha\approx+13°$.

was suggested[15] to result from a systematic error rather than from a real variation in the lattice constants of the different crystals used. As many of the x-ray wavelength measurements done over the last decade rely on the lattice constant of silicon for absolute calibration, a readjustment of these wavelengths will be required once the discrepancy is resolved. In particular, the MDCS Cu $K\alpha_1$ wavelength measurements of Deutsch and Hart[11] employed the National Bureau of Standards (NBS) value for the lattice constant of silicon. To put the present $K\alpha_2$ wavelength on equal footing with that study, Eq. (1) was not employed directly, but in a slightly different manner. Note that for two wavelengths $\lambda_1$ and $\lambda_2$ corresponding to angles $\alpha_1$ and $\alpha_2$, the ratio $\lambda_1/\lambda_2$ as calculated from Eq. (1) is completely independent from the crystal properties as represented by $d_1$ and $d_2$, and is a function of $\alpha_1$ and $\alpha_2$ only. Thus the wavelength of the $K\alpha_2$ line was calculated relative to that of $K\alpha_1$. A future readjustment of the silicon lattice parameter will shift both wavelengths by the same amount, leaving their *relative* values unchanged from the present study. Furthermore, such errors which influence both peaks (almost) equally, e.g., temperature variations during data collection and transverse beam divergence,[13] are reduced to insignificance. A refraction correction[17] was also applied. The axis of rotation was measured to be parallel to the [135] direction to better than 4 sec of arc, making the corresponding error negligible. The dominant contribution to the uncertainty in $\lambda(K\alpha_2)$ is that of the peak position determination, which is governed by the counting statistics,[18] and amounts in our case to 0.87 ppm. A noncumulative uncertainty of 2 sec of arc in the angular step size measured with an optical autocallimotor contributes a further 0.12 ppm. The temperature variations during data collection were $\sim0.5$ °C. As these variations were smooth and periodic with a periodicity much shorter than that of the total data collection time, their only effect is a negligible broadening of the line with no change in its peak position. Moreover, the positions of both the $K\alpha_1$ and $K\alpha_2$ peaks shift equally with temperature so that their *relative* angular positions, and hence their *relative* energy as calculated here, remain unchanged even for nonperiodic temperature variations. Finally, including the 0.85-ppm

uncertainty in the wavelength of the $K\alpha_1$ line we obtain

$$\lambda(\text{Cu } K\alpha_2) = 1.544\,425\,6 \pm 0.000\,001\,9 \text{ Å},$$

in excellent agreement with measured value of Deslattes and co-workers,[14] which is also based on the NBS value for the lattice constant of silicon. The accuracy in the wavelength corresponds to 1.2 ppm. This could be improved upon by using a higher-intensity rotating anode x-ray source, which will allow an order of magnitude increase in peak determination accuracy.

### B. Cu $K\alpha_2$ line shape

A measured $K\alpha_2$ spectrum is shown in Fig. 3. With one exception, eye inspection of the data and the numerical derivative method of Ref. 11 failed to indicate fine structure at consistent, equal energy positions on both the $\alpha < 0$ and $\alpha > 0$ peaks of the spectrum. The exception is a very small and wide shoulder on the low-energy side of the peak at a separation of 2.2 eV. This is close to, but somewhat smaller than, the 2.6 eV shift observed for a similar shoulder on the low energy side of the Cu $K\alpha_1$ line,[11] suggesting a common origin for both shoulders. The measured shifts are close to the values 2.1, 2.7 (Ref. 19), and 2.3 (Ref. 20) eV, calculated using various methods for the gap between the top of the 3*d* band and the Fermi level of Cu. This suggests a shake-up (or "radiative Auger") origin[21] for these shoulders, whereby a 3*d* electron is excited above the Fermi level simultaneously with the emission of the x-ray photon.

The double vacancy theory[10] predicts the center of gravity of the 3*d* spectator-hole multiplet associated with the $K\alpha_1$ and $K\alpha_2$ lines to lie approximately 2.5 and 2.2 eV to the low-energy side of the peaks. These values are also in good alignment with the positions of the shoulders. It should, however, be noted that no fine structure other than the shoulders is found in the data. In particular the measured curve is smooth on a scale of $\lesssim 1\%$ at the *high* energy side of the $K\alpha_1$ line and the low-energy side of the $K\alpha_2$ line at the positions predicted[10] for the strongest lines of the multiplet. Thus, while multivacancy effects were shown to play an important role both in the *K*-absorption[22] and $K\beta_{1,3}$-emission[23] processes, their manifestation as fine structure is absent from our data. The exchange interaction splitting theory[2] is also not supported by our data, as it predicts separations small compared to those of the shoulders. Moreover, it requires the existence of 3*d* holes in solid copper, contrary to the electron photoemission evidence.[24,11]

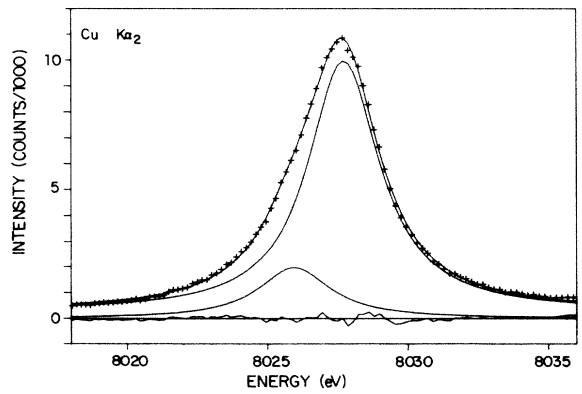


FIG. 3. Measured Cu $K\alpha_2$ spectrum (+) and its resolution into two DS-shaped components. The difference between the measured values and the fitted curve is also shown.

The measured FWHM, index of asymmetry,[13,8] and intensity ratio $I(K\alpha_2)/I(K\alpha_1)$ obtained from our data are listed in Table I along with previously published values. While the index of asymmetry of all measurements are in good agreement except that of Meisel and Nefedow,[25] the scatter in the FWHM is large. However, in the absence of error estimates for most of the published data, it is difficult to assess the real extent of the disagreement. The particularly low FWHM measured by Citrin *et al.*[1] using photon excitation cannot be attributed to the different mode of excitation, as the measured FWHM of the $K\alpha_1$ line is in good agreement with the measured electron excited linewidth.[11] The theoretical widths are consistently lower than the experimental ones. This reflects the difficulty of taking into account a variety of secondary excitation processes, surface induced splitting, phonon broadening, and other nonlifetime broadening mechanisms.[26,27]

The $I(K\alpha_2)/I(K\alpha_1)$ intensity ratio is in close agreement with almost all measured values and also with the theoretical relativistic Hartree-Slater calculations of Scofield.[28] The fluorescence yield $\omega_i$ is obtained from the measured x-ray linewidth $\Gamma_{K\alpha_i}$ through $\omega_i = \Gamma_{L_i}^{\text{rad}}/(\Gamma_{K\alpha_i} - \Gamma_K)$, where $\Gamma_{L_i}^{\text{rad}}$ and $\Gamma_K$ are the radiative level width of the $L_i$ shell and the total level width of the *K* shell, respectively. The values obtained for $\omega_2$ and $\omega_3$ from our present and previous[11] x-ray linewidths, $\Gamma_{L_i}^{\text{rad}}$ of Scofield[28] and $\Gamma_K$ from Refs. 26 and 29, are listed in Table II along with previous measurements and theoretical predictions. The agreement with the values derived from the measured x-ray linewidth of Lee and Salem[1] is satisfactory. The theoretical values, however, both nonrelativistic[30,31] and relativistic,[26] overestimate the experimentally derived ones, as expected from the nonlifetime broadening of the x-ray lines discussed above.

Finally, the shape of the $K\alpha_1$ line as measured with the present MDCS is identical with that of Ref. 11, and the width and index of asymmetry derived from the present $K\alpha_1$ data agree with those of Ref. 11 to well within their combined error estimates.

### C. Many-body effects in the line shape

The theory of Doniach and Sunjic[5] attributes the asymmetry of the iron-group x-ray emission lines to a Kondo-like many-body interaction of the conduction-band electrons with the final *L* hole states. The shape is further modified by the finite lifetimes of the *K* and *L* hole states, and is given by[5]

TABLE I. The Cu $K\alpha_2$ x-ray emission line FWHM, index of asymmetry, and $K\alpha_2$-to-$K\alpha_1$ intensity ratio.

| Source | FWHM (eV) | Asymmetry index | $I(K\alpha_2)/I(K\alpha_1)$ |
|---|---|---|---|
| Experimental | | | |
| Citrin *et al.*[a] | 2.89±0.10 | | |
| Tsutsumi and Nakamori[b] | 3.99 | 1.36 | |
| Parratt[c] | 3.31 | 1.28 | |
| Berger[d] | 3.39 | 1.36 | 0.479 |
| Lee and Salem[e] | 4.05±0.33 | 1.10±0.11 | |
| Obert and Bearden[f] | 3.28 | 1.33 | |
| Meisel and Nefedow[g] | 3.37 | 1.06 | 0.526 |
| Pessa[h] | 3.14 | | |
| Thomsen[i] | 3.34 | | |
| Bremer, Johnsen, and Sorum[j] | | 1.34 | |
| Salem and Wimmer[k] | | | 0.507 |
| McCrary *et al.*[l] | | | 0.511±0.01 |
| Present Work | 3.49±0.08 | 1.32±0.05 | 0.5077±0.0005 |
| Theoretical | | | |
| Citrin *et al.*[a] | 2.84 | | |
| Citrin *et al.*[m] | 3.00 | | |
| Krause and Oliver[n] | 2.17 | | |
| Scofield[o] | | | 0.513 |

[a]Reference 1.
[b]Reference 2.
[c]L. G. Parratt, Phys. Rev. **50**, 1 (1936).
[d]Reference 9.
[e]Reference 1.
[f]L. Obert and J. D. Bearden, Phys. Rev. **54**, 1000 (1938).
[g]Reference 25.
[h]V. M. Pessa, X-Ray Spectrom. **2**, 169 (1973).
[i]J. S. Thomsen, J. Phys. B **16**, 1171 (1983). This is a reanalysis of the data of J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).
[j]Reference 33.
[k]S. I. Salem and R. J. Wimmer, Phys. Rev. A **2**, 1121 (1970).
[l]J. H. McCrary *et al.*, Phys. Rev. A **4**, 1745 (1971).
[m]See note d in Table II of Ref. 1 (Citrin *et al.*).
[n]Reference 27.
[o]Reference 28.

TABLE II. Fluorescence yields $\omega_i$ for $L_2$ and $L_3$ levels of Cu. All widths are in eV.

| | FWHM | $10^3\Gamma_L^{rad}$ | $\Gamma_K$ | $10^3\omega_i$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Measured | | | Theoretical | |
| | | | | Present | Lee[a] | Yin[b] | McGuire[c] | Chen[d] |
| $L_3$ | 2.61±0.05[e] | 5.39[f] | 1.434[b] | 4.59±0.19 | 4.78±0.83 | 9.78 | 9.41 | 8.62 |
| $L_2$ | 3.49±0.08 | 5.50[g] | | 2.68±0.10 | 2.10±0.27 | 3.81 | | 8.71 |

[a]Reference 1.
[b]Reference 31.
[c]Reference 30.
[d]Calculated from total level widths of Ref. 26 and radiative widths of Ref. 28.
[e]Reference 11.
[f]$\Gamma_K^{rad}$ taken from Ref. 28 and $\Gamma_K^{nonrad}$ from Ref. 29.
[g]Reference 28.

TABLE III. The Cu $K\alpha_2$ lifetime width $\gamma$ and asymmetry parameter $\beta$ obtained from the fit of the DS theory to the data. $L$ and $R$ denote the $\alpha<0$ and $\alpha>0$ peaks, respectively, obtained in a single scan. For fitting procedures see the text.

| Fitted profile | $L$ | | | $R$ | | |
|---|---|---|---|---|---|---|
| | $\beta$ | $\gamma$ | $\sigma$ | $\beta$ | $\gamma$ | $\sigma$ |
| Single DS | 0.017 | 1.652 | 155.3 | 0.015 | 1.652 | 146.9 |
| Two DS | 0.0087 | 1.456 | 91.0 | 0.0096 | 1.460 | 90.7 |
| Lorentzian plus DS | 0.0069 | 1.465 | 91.5 | 0.0058 | 1.464 | 92.5 |

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

where $\Gamma$ is the usual gamma function, $E_0$ is the zero of the energy scale, $\gamma$ is the combined lifetime width, and $\beta$ is the asymmetry parameter. Equation (3) has the right qualitative form, a Lorentzian with a tail on its low-energy side. $\beta$ and $\gamma$, the parameters defining the exact shape, are determined by fitting Eq. (3) to the measured line. Note, however, that the shoulder appearing both on the $K\alpha_1$ and $K\alpha_2$ lines implies a two-line structure, rather than a single underlying line structure. Following Ref. 11, several approaches were tried.

(a) Fitting a sum of two DS profiles having equal $\beta$ and $\gamma$ to the measured data.

(b) Fitting the data by two skewed Lorentzians, as suggested by Tsutsuni and Nakamori.[2] This results in one of the Lorentzians being centered on the shoulder. This Lorentzian is subtracted from the data, which is then fitted by a single DS profile.

A fit of a single DS to the raw measured data was also attempted, resulting in an inferior fit. The $\beta$ and $\gamma$ values obtained are listed in Table III for the $K\alpha_2$ lines measured at $\alpha<0$ ($L$) and $\alpha>0$ ($R$), and a fit of the $K\alpha_2$ line to two DS profiles is shown in Fig. 3. The mean standard deviation $\sigma$ is also listed. Note that the $\beta$ values span a range of 200%, while those of $\gamma$ agree to $\leq 1\%$ excluding the value for a single DS profile; as indicated by the large $\sigma$, the single DS fit does not fit the data well. The large scatter in the $\beta$ values reflects the sensitivity of the DS profile to small changes in the low-energy tail of the line. We conclude, therefore, that while the DS theory as applied to our data yields a well-defined lifetime half width of $1.461\pm0.004$ eV, no well-defined value for $\beta$ can be stated. The measured electron photo emission width[1] of the $L_2$ level is $1.36\pm0.03$ eV, yielding a $K$-level width of $1.56\pm0.04$ eV, in excellent agreement with the 1.55-eV semiempirical value of Krause and Oliver[27] and the 1.52 theoretical relativistic value of Chen *et al.*[32]

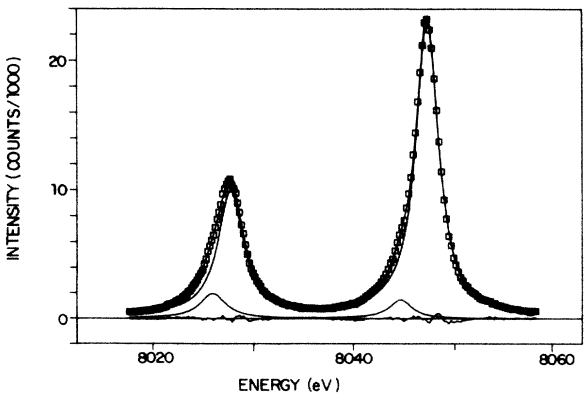


FIG. 4. Resolution of the complete measured spectrum into DS components. Note the almost equal heights of the minor components of the $K\alpha_1$ and $K\alpha_2$ lines. The difference between the measured data and the fitted curve is also shown.

In conclusion, the present study interprets the shape of the Cu $K\alpha_2$ line similarly to that of the $K\alpha_1$ line studied previously: a two-line structure with the second line resulting from shake-up of conduction-band electrons over the Fermi level. Each of the two component lines is asymmetrically broadened by a Kondo-type many-body interaction between conduction-band electrons and the final-state core hole. The resultant description fits both the $K\alpha_1$ and $K\alpha_2$ lines well, as shown in Fig. 4. One would expect the *relative* intensity of the shake-up components to be equal for the $K\alpha_1$ and $K\alpha_2$ lines. This is, however, not the case, as seen in Fig. 4. The minor components of the $K\alpha_1$ and $K\alpha_2$ lines are of roughly equal *absolute* intensity, i.e., the *relative* intensity of the $K\alpha_2$ minor component is twice as big as that of $K\alpha_1$. The same effect has also been noted by Bremer *et al.*[33] and is also present in Berger's[9] study. No equivalent problem arises for the multivacancy theory,[10] as the calculated intensity of the $3d$ multiplet lines associated with the $K\alpha_1$ and $K\alpha_2$ lines are about the same. Other problems, however, are outstanding for the multivacancy theory, as discussed above. Further high-resolution measurements on neighboring members of the iron-group elements are called for to establish structural trends in the lineshape, and thus elucidate the origin of the asymmetry and the underlying line structure of the iron-group elements.

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