Double-vacancy transitions in the copper $K\beta_{1,3}$ emission spectrum

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The β' and β'' satellites in the measured Cu $K\beta_{1,3}$ emission spectrum are shown to be due to the double-vacancy transitions $1s3p^6 3d^{9\,1,3}D \rightarrow 1s^2 3p^5 3d^{9\,1,3}PDF$. This assignment is consistent with an earlier analysis of a highly resolved Cu $K\alpha_{1,2}$ spectrum. The M_2 and M_3 level widths are estimated to be 1.68 eV, in agreement with 2.0 ± 0.3 eV and 1.6 ± 0.3 eV, respectively, from photoelectron spectroscopy, and a calculated width of 2.0 eV. Comparison of the calculated double-vacancy transition array with the neighboring elements $30 \leq Z \leq 32$ suggest a similar identification to the β' and β'' satellites in their $K\beta_{1,3}$ spectra.

INTRODUCTION

The $K\beta_{1,3}\beta'$ emission spectra of the first transition group metals have been investigated for some time both experimentally and theoretically.[1] The origin of the $K\beta_{1,3}\beta'$ profile for these elements is currently generally attributed to multiplet splitting of the open d-shell coupling to the K-shell vacancy. Comparison[2,3] with various calculations are in qualitative agreement with the multiplet model. In addition, a recent photon excitation measurement[4] of the Cr $K\beta_{1,3}\beta'$ at excitation energies of 21 and 57 eV greater than the Cr K binding energy of 5989 eV (the Cr $M_{2,3}$ binding energy is about 43 eV)[5] did not show any differences in the $K\beta_{1,3}\beta'$ profile. This photon excitation experiment supports the multiplet splitting model, since a difference in profile would indicate that the origin of the spectral differences was due to multiple vacancy transitions. The Cu $K\beta_{1,3}$ emission spectrum has two satellites,[6] β' and β'', on the low and high-energy side of the $K\beta_{1,3}$ peak position, respectively. However, these satellites are very weak relative to the β' contributions of the preceding transition elements. The absence of an open d shell for copper with a ground-state configuration of $3d^{10}4s$ and the relatively smaller intensity of $K\beta'$ in this case gives further support[2] to the multiplet model for those lower Z transition elements.

The more intense satellites in x-ray emission spectra have been attributed[7] to transitions between multiple vacancy configurations for some time. An example is the $\alpha'\alpha_3\alpha_4$ complex associated with the $K\alpha_{1,2}$ emission lines. For these satellites, the spectator vacancy is in one of the L subshells. Recently, it was shown[8] that the Ti $K\alpha'\alpha_3\alpha_4$ satellite complex is not present when the exciting photon energy is less than the Ti $K+L$ binding energy, in contrast to their presence when the photon energy is larger. Also, Chevallier *et al.*[9] have measured the $K\alpha_{1,2}$ of a number of $3d$ metals and found the linewidth to be dependent on the exciting photon energy. The variation in $K\alpha_{1,2}$ linewidth is ascribed to contributions of double-vacancy transitions with a spectator M shell vacancy that overlaps the region of the single-vacancy $K\alpha_{1,2}$ transition. A detailed illustration of this effect is the analysis of the highly resolved Cu $K\alpha_{1,2}$ spectrum obtained by Sauder *et al.*[10,11] with a novel monolithic double-crystal monochromator. The subtle structure in the measured spectrum was identified as mainly due to transitions of the double-vacancy states $1s2p^6 3d^{9\,1,3}D \rightarrow 1s^2 2p^5 3d^{9\,1,3}PDF$ and, to a lesser extent, $1s2p^6 3p^{5\,1,3}P \rightarrow 1s^2 2p^5 3p^{1,3}SPD$ superimposed on the prominent single-vacancy transitions $1s\,^2S \rightarrow 2p\,^2P$. The identification was supported by a synthesis of the spectrum with the multiplet structure calculated in intermediate coupling from a nonrelativistic Hartree-Fock calculation of the atomic hole states. As an extension to the analysis of the highly resolved Cu $K\alpha_{1,2}$ spectrum, I report here a similar consideration of the Cu $K\beta_{1,3}$ spectrum.

EXPERIMENTAL

The copper $K\beta_{1,3}$ spectrum was measured on a double-crystal monochromator[12] equipped with high-quality[13] Si(111) cut crystals. The copper $K\beta_{1,3}$ emission radiation was excited by electron bombardment in a sealed commerical tube at 31 kV and 6 mA. The measured Cu $K\beta_{1,3}$ spectral region is displayed in Fig. 1 without correction. This spectrum is very similar to the Cu $K\beta_{1,3}$ profile reported by Nikiforov and Blokhin.[14] The solid curve under and blending into the experimental points is a fitted distribution of two Lorentzians separated by 2.4 eV, with an intensity ratio of 2 to 1, and each with a full width at half-maximum (FWHM) of 5.0 eV. The solid curve is in-

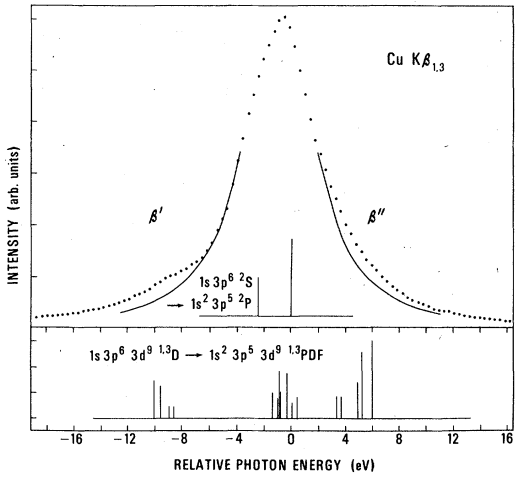

FIG. 1. Solid points are the experimental measurements of the copper $K\beta_{1,3}$ region without any corrections. The calculated Lorentzian profile depicting the (doublet) single-vacancy transitions is shown by the solid curve blending into the experimental profile. The lower line spectrum shows the distribution of the double-vacancy transitions $1s3p^63d^{9\,1,3}D \rightarrow 1s^23p^53d^{9\,1,3}PDF$.

tended to represent the single-vacancy transitions in the profile. Note that the Cu $K\beta_1$ (KM_3) component lies about 0.5 eV higher in energy than the peak position of the Cu $K\beta_{1,3}$ experimental peak. The weak bump in the −7 to −12 eV region is the β' satellite. The intensity contribution between the solid curve and the experimental points in the +3+10 eV region is the β'' satellite. The positions of β' and β'' are in agreement with the values measured by Bearden and Shaw,[6] namely, −8.4 eV and 6.3 eV, respectively.

RESULTS AND DISCUSSION

The emission intensity in the Cu $K\beta_{1,3}$ profile is mainly due to the (doublet) single-vacancy transitions $1s3p^63d^{10}\,^2S_{1/2} \rightarrow 1s^23p^53d^{10}\,^2P_{1/2,3/2}$. It is suggested that the β' and β'' satellites should be attributed to double-vacancy multiplet transitions $1s3p^63d^{9\,1,3}D \rightarrow 1s^23p^53d^{9\,1,3}PDF$. Model atomic calculations similar to the analysis of the Cu $K\alpha_{1,2}$ profile[11] were made to explore this possible identification. The model assumed that the ground state of the target copper atom is characterized as a $3d^{10}\,^1S_0$ Cu ion rather than a $3d^{10}4s\,^2S_{1/2}$ Cu atom, and that solid-state effects are negligible. Using the nonrelativistic Hartree-Fock program,[15] the initial and final hole states of the single and double-vacancy configurations were calculated to obtain the total energies and the Slater integrals. In Table I are listed some of the calculated parameters. The Slater integrals for the $3p^53d^9$ double-vacancy configuration are compared in Table II with other calculated values used in the literature for this configuration. The values of Mann[16] are for a neutral atom obtained with Hartree-Fock wave functions, which I have reproduced also for a neutral atom. McGuire's[17] values are for a neutral atom using Herman and Skillman[18] wave functions.

All the relevant hole state configuration energy matrices were diagonalized using the calculated Slater integrals and the spin-orbit interaction constants. In Table III is a comparison of the relative energies of the $3p^53d^9$ multiplet terms normalized to the $^3P_0$ with McGuire's[17] recent calculation. In view of the mixing, in the particular case of the $J=2$ terms, the listed energies refer to levels with 60% or more of the noted terms for the present calculation. The overall comparison is in good agreement with a small difference of about 1 eV, primarily due to the different values of the electrostatic interaction integrals used. The calculated total energy of each configuration was equated to the center of gravity of the individual levels of the multiplet to place all the calculated line spectra on the same energy scale, namely, the calculated energy scale of the spectrum. The experimental $K\beta_1$ (KM_3) transition is estimated to be 8905.8 eV, which

TABLE I. Calculated Hartree-Fock estimates of Slater-Condon parameters.

$1s3p^63d^{10}$	$1s^23p^53d^{10}$
Total energy −35,669.17 eV	Total energy −44,480.27 eV
$G_2(1s,3d)$ 0.088 37 eV	$G_1(3p,3d)$ 17.641 eV
$G_1(1s,3p)$ 3.543 eV	ζ_{3p} 1.5808 eV
$1s3p^63d^9$	$1s^23p^53d^9$
Total energy −35,631.43 eV	Total energy −44,443.96 eV
$G_1(1s,3p)$ 3.6189 eV	$G_1(3p,3d)$ 18.421 eV
$G_2(1s,3d)$ 0.096 66 eV	$G_3(3p,3d)$ 11.244 eV
ζ_{3d} 0.1387 eV	$F_2(3p,3d)$ 14.952 eV
	ζ_{3p} 1.6154 eV
	ζ_{3d} 0.1137 eV

TABLE II. Comparison of calculated electrostatic interaction integrals used for the $3p^5 3d^9$ configuration in Ry.

	$G_1(3p,3d)$	$G_3(3p,3d)$	$F_2(3p,3d)$
Ref. 16	1.215	0.7308	0.9808
Ref. 17	1.226	0.7410	
Present	1.354	0.8268	1.0994

is 0.5 eV greater than the $K\beta_{1,3}$ profile peak[5] at 8905.29 eV and greater than the calculated value of the $1s3p^6 3d^{10}\,{}^2S \rightarrow 1s^2 3p^5 3d^{10}\,{}^2P_{3/2}$, 8812.09 eV. This difference of 93.7 eV is primarily due to the use of nonrelativistic wave functions. A more complete relativistic relaxed orbital calculation by Huang *et al.*[19] gives a value of 8899.18 eV for this transition.

The relative strengths[20] in intermediate coupling were obtained by transformation of the transition arrays from pure *LS* coupling. The resulting electric dipole transition spectrum for $1s3p^6 3d^{9\,1,3}D \rightarrow 1s^2 3p^5 3d^{9\,1,3}PDF$ consisted of 36 lines. The strengths of individual lines whose positions were within an interval of 0.15 eV were summed to give an array of 16 lines, shown in Fig. 1; also shown are the single-vacancy doublet transitions. The line spectrum energy scale zero corresponds to the peak of the Cu $K\beta_1$ (KM_3) Lorentzian component of the calculated solid curve in Fig. 1.

A comparison of the line spectrum and experimental profile shows a direct correspondence of the β' and β'' satellite to the calculated double-vacancy transitions on both sides of the peak position. The strongest two transitions in the calculated β' region are from weakly mixed $^1F_3$ terms, and the two lesser transitions are from weakly mixed $^1P_1$ terms. The relative prominence of the experimental β' compared to β'' is ascribed to the tighter clustering of the double-vacancy transitions in this region and their appearance further along on the tail of the stronger single-vacancy transition. The double-vacancy transitions $1s3p^5 3d^{10\,1,3}P \rightarrow 1s^2 3p^4 3d^{10\,1,3}SPD$ would be present also under the experimental conditions used to measure the Cu $K\beta_{1,3}$ spectrum. These transitions would be distributed on the high-energy side of the peak position, but less probable than $1s3p^6 3d^9 \rightarrow 1s^2 3p^5 3d^9$ transitions. On the low-energy side of the peak there could also be contributions due to shake-up processes, which would be weak.

The experimental total level widths for M_2 and M_3 levels are each about 1.68 eV. These values were obtained by subtracting the initial-state Cu $K(1s)$ level width[11,21,22] of 1.48 eV and an instrumental broadening of 1.84 eV, obtained from the FWHM of the Si(111) rocking curve, from the 5.0-eV FWHM of the individual Lorentzians used to fit the single-vacancy contribution of the spectrum in Fig. 1. A comparison with the M_2 and M_3 level widths obtained by photoelectron spectroscopy, 2.0 ± 0.3 eV and 1.6 ± 0.3 eV, respectively, and the calculated level widths of $M_{2,3}$ of 2.0 eV by Yin *et al.*[23] and McGuire[17] are in good agreement.

TABLE III. Comparison of the relative energies of the terms within the double-vacancy configuration $3p^5 3d^9$ of Cu in eV.

Term	E_{rel} [a]	E_{rel}
$^3F_4$	5.11	5.67
$^3F_3$	4.22	4.56
$^3F_2$	3.55	2.93
$^1F_3$	−9.02	−10.36
$^3D_3$	−1.09	−1.28
$^3D_2$	−1.42	−1.49
$^3D_1$	−1.64	−2.18
$^1D_2$	3.59	4.62
$^3P_2$	−0.87	0.62
$^3P_1$	−0.21	0.22
$^3P_0$	0.13	0.13
$^1P_1$	−7.85	−9.24

[a] Reference 17.

The above interpretation of the Cu $K\beta_{1,3}$ spectral region can be extended to the next few elements. This would seem reasonable since these $3d^{10}$ ion core elements all would have Slater integrals of comparable values, but a spin-orbit splitting ranging up to twice the value for copper. The β' and β'' positions for $29 \leq Z \leq 32$ elements measured by Bearden and Shaw[6] are shown in Fig. 2. Note that the relative position of β' and β'' from their respective $\beta_{1,3}$ or β_1 are all displaced about the same distance. The extension of the present interpretation of the β' and β'' satellites for these elements appears to be consistent except for the Ge spectrum, which does not exhibit a Ge $K\beta'$ satellite. It is suggested that the ab-

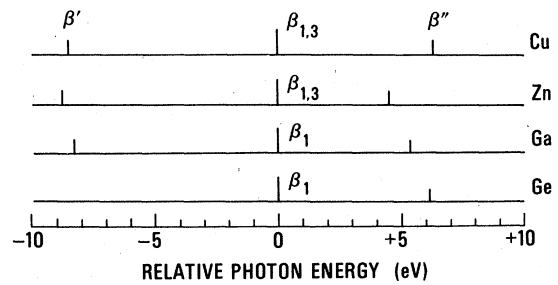

FIG. 2. Comparison of the positions of β' and β'' relative to their parent $\beta_{1,3}$ or β_1 position for the elements ${}_{29}\text{Cu} \leq Z \leq {}_{32}\text{Ge}$.

sence of a Ge $K\beta'$ satellite in the measurements is not an absence of the satellite in the spectrum but a difficulty in its detection relative to the Cu $K\beta'$ feature, for example. Since the $M_{2,3}$ spin-orbit splitting of Ge is about 5.0 eV, the broad distribution of Ge $K\beta'$ satellite would be positioned about halfway up the low-energy side of Ge $K\beta_{1,3}$ and would probably be obscured by the Ge $K\beta_3$ shoulder.

CONCLUSION

The origin of the β' and β'' satellites of Cu $K\beta_{1,3}$ emission line has been identified as being due to the double-vacancy transitions $1s3p^63d^9\,{}^{4,3}D \rightarrow 1s^23p^53d^9\,{}^{4,3}PDF$. This identification is in accord with the interpretation of the subtle structure[11] of the Cu $K\alpha_{1,2}$. An extension of this analysis to the identification of the β' and β'' of the elements $30 \leq Z \leq 32$ has also been suggested with fair agreement.

The 3d elements of less than $Z = 29$ (Cu) normally have open $3d$ shells. Thus the x-ray emission spectra obtained by the usual procedure of bombardment with excess energy would contain the superposition of the single and multiple-vacancy multiplets. To sort out the contributions with the aid of the present models at hand is still very difficult and uncertain. The most practical procedure is to first obtain high-resolution emission spectra at controlled excitation energies as described in the preliminary investigations of Refs. 8 and 9. These so-called "clean" emission spectra obtained at just above the threshold of the different possible initial states would be much easier to compare with model calculations.

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