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BRIEF REPORTS

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$K\alpha_{1,2}$ x-ray emission and Doniach-Šunjić-type line shapes

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The $K\alpha_{1,2}$ x-ray emission spectra of potassium chloride as well as metallic potassium, calcium, and iron have been measured and analyzed. A Doniach-Šunjić-type line shape is introduced in order to find well-behaved Lorenzian-like tails for the spectra. Furthermore, the obtained many-body effects and lifetime broadenings are considered in the light of theoretical estimates. [S0163-1829(99)04305-2]

I. INTRODUCTION

The earliest high-resolution x-ray emission (XES) $K\alpha_{1,2}$ lines of calcium have been measured by Parratt.[1] However, so far the corresponding potassium spectra have been obtained from compounds only.[2] From the point of x-ray microanalyses the $K\alpha_{1,2}$ lines are the most important ones. Also, other fields of applied as well as basic sciences are using this spectroscopy.[3] Therefore, it is worthwhile to consider these spectra in order to find an analytic expression for the line shape. In the case of $K\alpha_1$ and $K\alpha_2$ spectra the $1s$ hole moves to the $2p_{3/2}$ and $2p_{1/2}$ states, respectively, and an x-ray quantum is emitted. If one does not take into account the interaction between the created core hole and the conduction electrons, the XES line would be of the form of Lorentzian. However, in metals the response of the conduction electrons to the deep hole makes the line shape asymmetrical. The spectrum has a tail on the low energy side of the line because a part of the photon energy goes into excitation of electron-hole pairs at the Fermi surface.[4] The main question is, whether we can obtain an adequate description of the effect of the many-electron screening response on the x-ray emission line shape. The Doniach-Šunjić expression[5] has been shown to give reliable life-time widths for the core holes, but less successful results for the asymmetry of the spectrum.[6,7] The observation that the $K\alpha_1$ line of metallic iron is strongly asymmetrical seems to be difficult to understand. This property has been ascribed to the many-body screening effects,[5] due to the $2p$ core hole in the final state or to the intra-atomic exchange interaction between the $2p$ hole and the partially filled $3d$ level, which causes a splitting of the line.[8] It is now shown that the spectrum is well described by the former phenomena, which was originally suggested by Parratt.[5] The tails of the line-shape function play an important role in the determination of the singularity index, which is associated with the asymmetry of the line.[4,5] If these tails are not properly considered, the extraction of the parameters from the experiment is not unambiquous.[6,7]

II. EXPERIMENTAL DETAILS

The measurements were made with a two crystal vacuum spectrometer using two Si(111) crystals.[9] The emission experiments were performed with a Cr tube (30 kV, 30 mA). The radiation was detected by means of an argon-methane gas flow proportional counter. The potassium and calcium samples were made of high-purity metals. To ensure cleanliness of the specimen, it was covered by a thick (20 μm) polypropylene foil on both sides. This film was then mounted on a water-cooled sample holder that had two gaskets between which the sample was pressed. After three days in the pressure of 10^{-3} Torr there were no detectable sign of oxidation. The KCl and Fe samples were commercial ones. In the case of iron the full width at half maximum (FWHM) of the rocking curve in the $(3,-3)$ position was less than 0.05 eV, whereas for potassium and calcium it was (in the $(1,-1)$ position) 0.40 and 0.45 eV, respectively. The shape of the instrumental function is usually assumed to be between Lorentzian and Gaussian.[10] In the following, the latter one is supposed to be small and therefore pure Lorentzian shape is used for the instrumental broadening. This approximation is motivated by the high resolution of the measurements.

III. LINE SHAPE

A many-body spectrum for soft x-ray emission valence bands of simple metals, close to the Fermi level, has been suggested by Mahan,[11] which turns to a one-body expression at lower energies from the threshold. This means that the effect of the core-hole would have a very small contribution to the shape of the x-ray emission bands away from the neighborhood of the Fermi level.[12,13] The exponential, energy-dependent ''cutoff'' function, which is multiplied by a power-law singularity due to the electronic many-body effect, is caused by the joint density of states and transition matrix elements.[11] The later ones are often assumed to be constants.[14] Using the arguments given by Hopfield[15] as well as Combescot and Nozières[16] the power law with the effect of the joint density of states, due to electron-hole pair excitations,[11] can be converted to the $K\alpha_{1,2}$ line spectra, too. Roughly speaking, the atom (with the core hole) in the ground state does not affect much the conduction electrons whereas the excited atom in the final state will create a scattering potential, which gives phase shifts $-\delta_l$ for these electrons.[15] The asymmetry of the $K\alpha_{1,2}$ line is caused by Auger-like excitations at the Fermi level.[16]

The power law can be generalized to include the Lorentzian broadening, which describes the life-time effect of the core holes.[5] Hence, using the Gadzuk-Šunjić integral,[17] the obtained many-body spectrum can be written as the following convolution:

$$I(E) \propto \int_0^\infty \frac{1}{\pi} \frac{\gamma}{(E+E')^2+\gamma^2} \frac{e^{-E'/\xi}}{E'^{1-\beta}} dE', \qquad (1)$$

where 2γ denotes the lifetime width and ξ is a cutoff energy, which is of the order of magnitude 6–8 eV.[18,19] Furthermore, Combescot and Nozières have shown that

$$\beta = 2\sum_{l=0}^{\infty} (2l+1)\left[\frac{\delta_l}{\pi}\right]^2 \qquad (2)$$

describes the singularity index[16] and the phase shifts obey the Friedel sum rule

$$\frac{\pi}{2} = \sum_{l=0}^{\infty} (2l+1)\delta_l . \qquad (3)$$

Since integral (1) has been difficult to solve analytically,[17] we assume narrow x-ray emission lines in the sense that $\gamma/\xi \rightarrow 0$ and that the high-energy side of the spectrum is a Lorentzian. The line shape is now of the approximate Gadzuk-Šunjić (Ref. 17) form

$$I(E) \propto e^{(E-|E|)/2\xi_0} \frac{\Gamma(1-\beta)}{(E^2+\gamma^2)^{(1-\beta)/2}} \times \cos\left\{\frac{\pi\beta}{2} + (1-\beta)\arctan\left(\frac{E}{\gamma}\right)\right\}, \qquad (4)$$

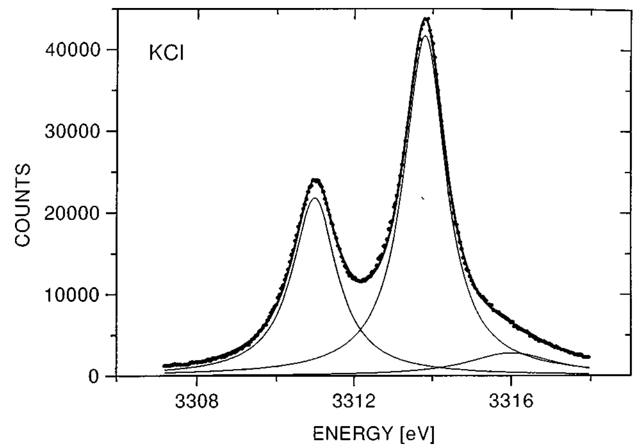

FIG. 1. The $K\alpha_{1,2}$ spectrum of K in KCl. The fitted Lorentzians are shown, as well. The spin-orbit splitting energy is 2.8 eV.

where $\xi_0 \cong \xi$. On the low energy side of the line, the effect of the joint density of states, which is included in $e^{(E-|E|)/2\xi_0}$, makes the tail, far away from the neighborhood of the singularity, more Lorentzian as compared with the standard Doniach-Šunjić line shape.[5,17] The reason is that the singularity index has been approximated by the expression[11,14] $\beta(E') = \beta e^{-E'/\xi}$, for $E' > 0$ and approaches zero for $E' \rightarrow \infty$. Hence, $\beta(E)$ will decrease on going to lower photon energies. One can say that by introducing a cut off factor the exponent (2) will be energy dependent.[14,20] The integral (1) takes now the form

$$I(E) \propto \int_0^\infty \frac{1}{\pi} \frac{\gamma}{(E+E')^2+\gamma^2} \frac{1}{E'^{1-\beta(E')}} dE', \qquad (5)$$

In the case of $\beta(E) = \text{const}$ the usual Doniach-Šunjić line shape[5] is found. The asymmetry of the line is due to the final state effect, because there exists a more pronounced tail on the low-energy side of the spectrum.

IV. RESULTS

The potassium $K\alpha_{1,2}$ line from KCl is shown in Fig. 1. On the high-energy side of the spectrum a satellite is found, which is largely caused by the $1s^{-1}3p^{-2} \rightarrow 2p^{-1}3p^{-2}$ transition.[2] The fitted Lorentzians for the main lines posses the full width at half-maximum (FWHM) $2\gamma = 1.35 \pm 0.10$ eV and that of the satellite 3.40 ± 0.20 eV. Subtracting the instrumental broadening from the spectra, a natural width of 0.95 ± 0.1 eV is obtained for the $K\alpha_1$ and $K\alpha_2$ lines, which is only slightly larger than the theoretical one 0.87 eV.[21] Moreover, constant background subtraction has been used.

Figure 2 shows the $K\alpha_{1,2}$ lines for metallic potassium. Although these lines are somewhat broader than those for KCl, the lifetime widths are still the same. The reason is the extra broadening on the low energy side of the spectra, which is caused by the many-body effect. Table I gives the parameters in question. Our experimental index $\beta = 0.14 \pm 0.02$ is in good overall agreement with the theoretical estimate[22] 0.12 as well as with the recent x-ray photoemission (XPS) result 0.14 ± 0.01 for the K $3p$ lines.[23] It should be noted that the high-energy satellite is assumed to have the same singularity index as the main lines. The small deviation

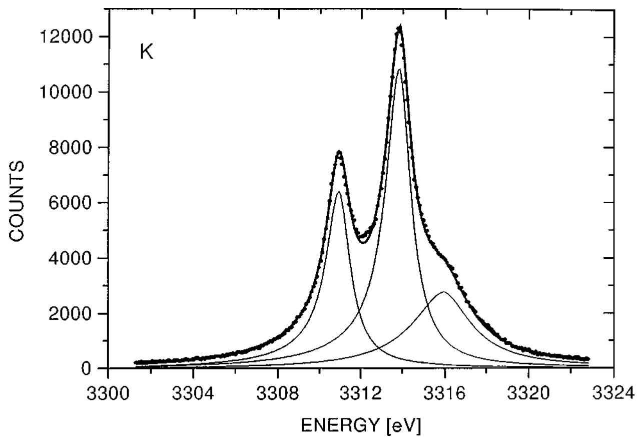

FIG. 2. The $K\alpha_{1,2}$ doublet for metallic potassium. The spin-orbit splitting energy is 2.9 eV. The asymmetric line shapes exhibit the many-body effect.

in the middle between the $K\alpha_1$ and $K\alpha_2$ lines as far as the fitted curves and the measurements are concerned, is due to a small satellite,[24] which is, however, not visible in the case of the KCl spectra in Fig. 1.

Our experimental calcium $K\alpha_{1,2}$ spectrum is very similar to that measured by Parratt.[1] The spin-orbit splitting energy is 3.6 eV. The estimated lifetime width is now 1.0 ± 0.1 eV, which agrees well with the corresponding theoretical one[21] 0.95 eV. The singularity index $\beta=0.15\pm0.02$ is in good agreement with the spin symmetric calculation[25] for the Ca $2p$ line, which gives 0.146.

The iron $K\alpha_1$ emission line is shown in Fig. 3. The fit is excellent and gives $\beta=0.36\pm0.03$, which is much larger than those obtained for simple metals. The reason is screening of the $2p$ hole due to more localized d-like electrons. The lifetime broadening is now 1.82 ± 0.10 eV, which can be compared with the theoretical estimate 1.58 eV.[21] One should note the very Lorentzian-like tail on the high-energy side of the spectrum.[26] It is evident that the many-body effect gives a strong contribution to the asymmetry of the line. The deviation from the asymptotic power law is not solely due to the energy dependent exponent $\beta(E)$, but also to the core-hole potential strength. Cox *et al.*[27] have shown that a stronger potential gives rise to a larger deviation from the standard Doniach-Šunjić line-shape function.

V. COMPARISON WITH THE FELDKAMP-DAVIS LINE SHAPE

Some years ago Feldkamp and Davis proposed a discrete solution for the x-ray edge model.[28] In the case of XPS core-level spectra, their result is different from the usual asymptotic power law in the sense that they introduced a negative step function below threshold of the line. By convoluting the line with a Lorentzian, one finds a spectrum, which has the property that the tail on the low-energy side decreases more rapidly than that of the standard Doniach-Šunjić form.[28] The convoluted Feldkamp-Davis (FD) expression can be approximated by subtracting from the Doniach-Šunjić (DS) spectrum a background, which actually is a Lorentzian broadened step function.[29] [Another way to have formally the same result is to assume that $\xi\gg E$ and $\beta\rightarrow0$ in (1).] The line shape is now of the form

$$I_{\rm FD}(E)\cong I_{\rm DS}(E)-\frac{1}{\xi\pi}\left[\frac{\pi}{2}-\arctan\left(\frac{E}{\gamma}\right)\right], \qquad (6)$$

where ξ is a constant, which is connected with the cutoff distance of the low-energy tail in the spectrum. For the Fe $K\alpha_1$ line the fitted spectrum is shown in Fig. 4. The obtained parameters are $\beta=0.33\pm0.03$, $2\gamma=1.86\pm0.10$ eV, and $\xi=5.8$ eV, by assuming the area of the Feldkamp-Davis spectrum $I_{\rm FD}(E)$ to be one. The singularity index is just slightly smaller than that in Table I. The fit is also similar to that in Fig. 3, except for far away on the low-energy side of the line, where a small deviation can be seen. It is evident that values of β are not very dependent on the model function, which is

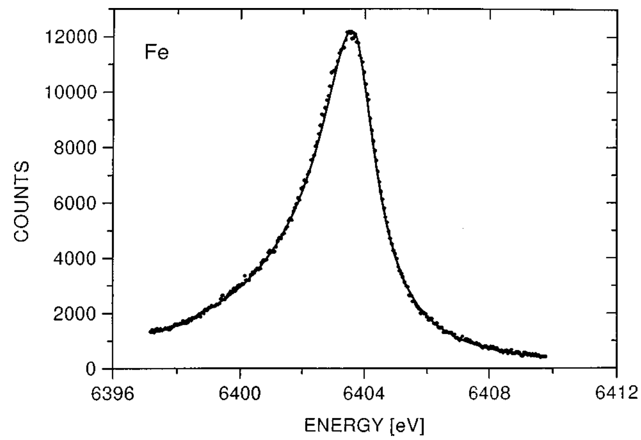

FIG. 3. The $K\alpha_1$ line for iron with the fitted line shape.

TABLE I. The singularity index β, broadening 2γ and constant ξ_0, which is connected with the joint density of states, are shown for KCl, K, Ca, and Fe.

	KCl	K	Ca	Fe
β	0	0.14 ± 0.02	0.15 ± 0.02	0.36 ± 0.03
2γ (eV)	1.35 ± 0.10	1.35 ± 0.10	1.45 ± 0.10	1.82 ± 0.10
ξ_0 (eV)	∞	6.5	7.0	6.2

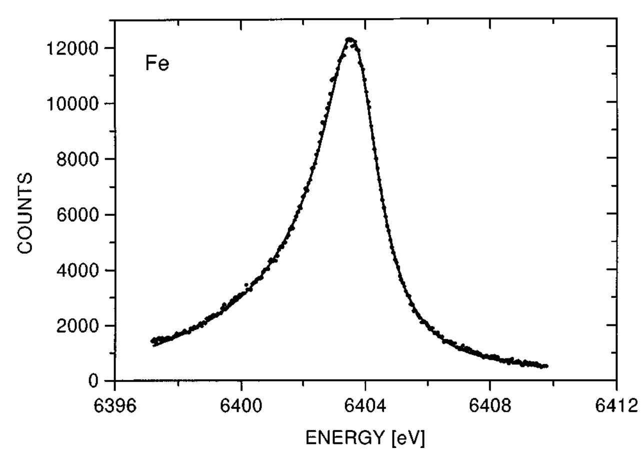

FIG. 4. The Fe $K\alpha_1$ spectrum fitted with the Feldkamp-Davis line shape.

used to fit the data provided the approximate line shape in question is sufficiently accurate.

VI. DISCUSSION

One can consider the XES line spectra as being due to a two step process.[16] During the ionization of the atom in the metal, a core-hole potential V_i is created for a deep level. The next step will be the transition of the hole from the deeper level to the higher level and the x-ray quantum is emitted. After the x-ray emission the dynamical scattering potential is of the form $V_f = V_i - V$ in the final state, where V is the transient potential that will change the phase shifts of conduction electrons[16] and causes the asymmetry of the spectrum. The latter one takes now the form $V_f - V_i = (V_i - V) - V_i = -V$, which is in line with Hamiltonian (5) in Ref. 16. In the case of the $K\alpha$ lines the scattering potential V_i is caused by the $1s$ core-hole and V is due to the $2p$ core-hole. The final state potential V_f is just the difference between the $1s$ and $2p$ scattering potentials. Since there exists initially the $1s$ hole, only the $2p$ core-hole gives the scattering phase shifts, which are included in Eqs. (2) and (3). One can assume the many-body line shape $e^{-E/\xi}(\xi/E)^{1-(\delta_f/\pi - \delta_i/\pi)^2}$ for $E > 0$,[14] in which the scattering phase shift δ_i for an s wave $(l=1)$, without spin, is due to V_i and the final-state phase shift δ_f in the same way is associated with the dynamical scattering potential V_f, respectively.[15] In the case of the XES line-emission spectra, the ''initial'' state also has a core hole. Since the final state perturbing potential is equal to the ''initial'' state potential minus the scattering potential,[16] one has the phase shift $\delta_f = \delta_i - \delta$, where δ is caused by the scattering potential V. The asymmetry of the emission line arises, because the influence of the initial core hole, which is assumed to be present all the time, is subtracted from the difference between screening charges, when the core hole moves from a deeper level to a higher level in the final state. Therefore, the singularity index can be written as $\beta = (\delta_f/\pi - \delta_i/\pi)^2 = (-\delta/\pi)^2$. This is in contrast with the weak-coupling result of Doniach-Šunjić[5] neglecting the effect of the initial core hole by considering the screening charge differences between the two deep holes only.

A distinction between the XPS and XES line-emission processes can be considered.[16] The former one has no core hole in the initial state, which means that the deep levels are fully occupied by electrons and therefore $\delta_i = 0$, whereas $\delta_f = \delta$ because of the screening cloud in the final state. The XPS singularity index α takes now the form $(\delta_f/\pi - \delta_i/\pi)^2 = (\delta/\pi)^2$ for s-phase shifts, which is very similar to β. Although the dynamical process for the XPS and XES line spectra deviate from each other, the singularity indices α and β, nevertheless, are not very different.

Considering the exponents of the absorption (or emission) and line emission spectra, one can write $\delta_l = \pi/2\,(\alpha_l + \beta)$ for the scattering phase shifts.[30,16] As far as potassium is concerned, the extracted threshold exponent $\alpha_0 = 0.23$ from the soft x-ray absorption spectrum[31] can be combined with the singularity index $\beta = 0.14$, which gives $\delta_0 = 0.58$ for the s-wave scattering phase shift being only slightly smaller than the corresponding theoretical estimate[22] $\delta_0 = 0.63$. This good overall agreement between theory and experiment clearly shows the importance of the s-wave scattering in the case of metallic potassium.

For the iron emission line, one can conclude that a considerable part of the FWHM is ascribed to the many-body screening effect, since beta is so large in this case. Also, the obtained lifetime broadening agrees reasonably well with the previously found theoretical estimate.[21] Regarding the deviation between the true line shape and the asymptotic power law, our study finds evidence that not only the energy-dependent singularity index $\beta(E)$, but also the increasing core-hole potential strength lowers the tail on the low energy side of the $K\alpha_1$ spectrum.[27]

As a conclusion we emphasize that in many cases it is possible to extract many-body singularity indices from the experimental x-ray $K\alpha_{1,2}$ spectra of metals, provided the $2p$ spin-orbit splitting energy is sufficiently large. XES is a bulk sensitive method, which allows reliable estimates for these parameters.

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[1] L. G. Parratt, Phys. Rev. **49**, 502 (1936).
[2] J. Kawai, C. Satoko, and Y. Gohshi, J. Phys. C **20**, 69 (1987).
[3] T. Åberg, Nucl. Instrum. Methods Phys. Res. B **87**, 5 (1994).
[4] P. W. Anderson, Phys. Rev. Lett. **18**, 1049 (1967).
[5] S. Doniach and M. Šunjić, J. Phys. C **3**, 285 (1970).
[6] M. Deutsch and M. Hart, Phys. Rev. B **26**, 5558 (1982).
[7] N. Maskil and M. Deutsch, Phys. Rev. A **37**, 2947 (1988).
[8] V. M. Pessa, Phys. Rev. B **15**, 1223 (1977).
[9] M. H. Heinonen, J. A. Leiro, and E. J. Suoninen, Philos. Mag. **44**, 175 (1981).
[10] J. Schweppe, R. D. Deslattes, T. Mooney, and C. J. Powell, J. Electron Spectrosc. Relat. Phenom. **67**, 463 (1994).
[11] G. D. Mahan, Phys. Rev. B **11**, 4814 (1975).
[12] C. A. Swarts, J. D. Dow, and C. P. Flynn, Phys. Rev. Lett. **43**, 158 (1979).
[13] L. C. Davis and L. A. Feldkamp, Phys. Rev. B **23**, 4269 (1981).
[14] G. K. Wertheim and L. R. Walker, J. Phys. F **6**, 2297 (1976).
[15] J. J. Hopfield, Comments Solid State Phys. **2**, 40 (1969).
[16] M. Combescot and P. Nozières, J. Phys. (Paris) **32**, 913 (1971).
[17] J. W. Gadzuk and M. Šunjić, Phys. Rev. B **12**, 524 (1975).
[18] P. Longe, Phys. Rev. B **8**, 2572 (1973).
[19] A. Fujimori, Y. Onuki, T. Komatsubara, and S. Sato, Phys. Rev. B **37**, 10 357 (1988).
[20] P. Minnhagen, J. Phys. F **7**, 2441 (1977).
[21] D. L. Walthers and C. P. Bhalla, Phys. Rev. A **4**, 2164 (1971).
[22] G. W. Bryant, Phys. Rev. B **19**, 2801 (1979).
[23] G. K. Wertheim and D. M. Riffe, Phys. Rev. B **52**, 14 906 (1995).
[24] T. Åberg (private communication).
[25] T. T. Rantala, Phys. Rev. B **28**, 3182 (1983).

[26] T. Papp and J. L. Campbell, Nucl. Instrum. Methods Phys. Res. B **114**, 225 (1996).
[27] D. L. Cox, H. O. Frota, L. N. Oliveira, and J. W. Wilkins, Phys. Rev. B **32**, 555 (1985).
[28] L. A. Feldkamp and L. C. Davis, Phys. Rev. B **22**, 4994 (1980).
[29] G. K. Wertheim, Phys. Rev. B **25**, 1987 (1982).
[30] P. Nozières and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).
[31] T. Ishii, Y. Sakisaka, S. Yamaguchi, T. Hanyu, and H. Ishii, J. Phys. Soc. Jpn. **42**, 876 (1977).