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Tellurium valence-band x-ray spectrum $L\gamma_4$ ($L_1O_{2,3}$)

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The profile of the Te $L\gamma_4$ ($L_1O_{2,3}$) x-ray emission spectrum has been measured using direct electron bombardment. Comparison of this valence-band x-ray spectrum with recent band calculations and photoemission spectrum are in general agreement. Certain differences are nevertheless noted between the observed profile and that expected on the basis of symmetry-weighted density of states. This departure is attributed to the quasiatomic character of the x-ray emission process and illustrates one limitation of the general practice of obtaining density of states from x-ray emission spectra. An emission line was observed also at 4898.9 ± 0.4 eV, which has tentatively been identified as the quadrupole transition Te($L_1N_{4,5}$).

I. INTRODUCTION

Tellurium has been the subject of several different types of investigations over a number of years.[1] At present, it is generally accepted that the valence band is of mixed *s* and *p* character; however, there has been considerable discussion on the extent of the hybridization.[2,3] Recently, Joannopoulos *et al.*[4] have made extensive calculations using empirical pseudopotentials and tight-binding models for Se and Te in crystalline and amorphous states, in which small amounts of *s* and *d* admixture to the *p*-like valence bands were used in the models. The resulting calculated densities of states were found to be in good agreement with recent photoemission measurements.[5]

In principle, the valence band of Te can be studied also be x-ray emission. The most useful valence band to probe would be the *p*-like system made up mostly of 5*p* electrons ($O_{2,3}$ shell). Earlier measurements of the Te $L\gamma_4$ ($L_1O_{2,3}$) spectrum were reported in 1922 by Coster[6] and in 1941 by Haglund,[7] both using photographic detection. The Te $L\gamma_4$ wavelength tabulated by Bearden[8] is the same as the measurement obtained by Haglund.[7] Noreland and Ekstig[9] repeated this measurement as part of a study of L emission for $_{46}\mathrm{Pd}\leqslant Z\leqslant{}_{52}\mathrm{Te}$, recording the spectra by photon counting. Their measured $L\gamma_4$ ($L_1O_{2,3}$) profile does not reflect the valence-band structure of Te, and suggested a reinvestigation of the x-ray emission spectrum in the $L\gamma_4$ ($L_1O_{2,3}$) region.

II. EXPERIMENT

The x-ray emission spectrum was produced by direct electron bombardment in a demountable x-ray tube[10] in which the bombarding electrons are incident normal to the anode target and the observed photons emerge along the same normal. The Te target was prepared by rubbing a commercially obtained single crystal of Te on a copper anode that had previously been roughened with coarse abrasive. The measurements were made using a vacuum double crystal monochromator[11] equipped with high-quality silicon (220) crystals. The radiation was detected with a flowing gas proportional counter using P10 gas (0.9 Ar + 0.1 CH_4) at 600 Torr. The x-ray tube operated at 11 kV and 85 mA during the measurements.

The measured Te $L\gamma_4$ ($L_1O_{2,3}$) spectrum is shown in Fig. 1. The data points are averages of three separate scans with a total of 300 sec of counting time per data point. The energy scale was set by an absolute measurement[12] of the angle and using $2d_\infty = 3.840\,341\,4$ Å (Ref. 13), and $\delta/\lambda^2 = 3.22\times10^{-6}$ Å^{-2} (Ref. 14), to give a $2d_{\mathrm{eff}} = 3.840\,159\,0$ Å for the silicon (220) crystals. The value of 12 398.12 Å eV was used to convert the scale to electron volts. The full width at half-maximum (FWHM) of the rocking curve in the spectral region of Fig. 1 was measured to be 0.42 eV.

III. RESULTS

The measured Te $L\gamma_4$ spectrum (Fig. 1) appears as a peak with a shoulder on its high-energy side.

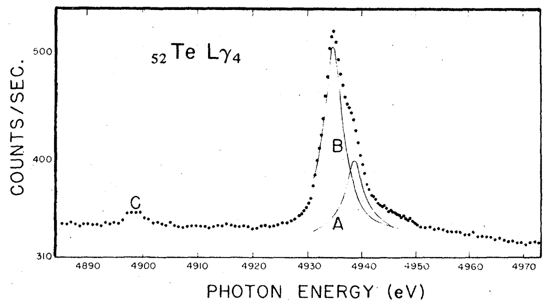

FIG. 1. $L\gamma_4$ emission spectrum of $_{52}$Te obtained by direct electron bombardment.

A graphical decomposition of the spectrum into two components is shown in the figure. Also of significance is the intensity distribution from 4940 to about 4965 eV, which is attributed to multivacancy transitions (satellites). The profile reported by Noreland and Ekstig[9] consists of a skewed peak that falls off relatively more slowly on the low-energy side. In another paper, Noreland[15] comments regarding the Te $L\gamma_4$ measurement that "an indication of a double peak was found during the recording of the Te L_1 emission band." However, the reported profile does not indicate a double peak, which may be attributed to the lower resolution, 0.91 eV, and there was no evidence of the satellite structure in the 4940-to-4965 eV region.

An estimate of the target self-absorption can be made by determining the average depth d for the production of the x-ray continuum. The ratio of the total number of counts at points 4919 and 4971 eV, I_L and I_H, respectively, is 1.043 ± 0.006. Reference 9 reports for the ratio at two points situated around 10 XU on each side of the $L\gamma_4$ line a value of 1.042 ± 0.011. Note that 10 XU, which is equal to about 20 eV, on the high-energy side is in the region of the satellite structure and would give an erroneous estimate of I_H. Assuming that the average depth d is the same at both points then

$$I_L = I_H \exp(\mu_H - \mu_L)d\,,$$

where μ_h and μ_L are the mass absorption coefficients and $d = \rho t$, with ρ the density (g/cm^3) and t the thickness (cm). A value of $d = 3.8 \times 10^{-4}$ g/cm^2 is obtained by using $\mu_H = 950$ cm^2/g and $\mu_L = 840$ cm^2/g from Ref. 16. The self-absorption on the high-energy side is estimated to be about 4% greater than on the low-energy side of the $L\gamma_4$ profile in Fig. 1. This minimal amount of self-absorption should not distort the $L\gamma_4$ profile unduly.

The wavelength position of the $L\gamma_4$ peak maximum is listed together with Haglund's value[7] in Table I. Reference 9 does not tabulate the peak position, but from the profile it appears that the position of the Te $L\gamma_4$ peak maximum is comparable to Haglund's measurement. The peak position discrepancy is primarily a discrepancy in the measured line profile. It is also possible that the measurements being compared may have been from different target materials, i.e., oxidized or alloyed tellurium as well as, possibly, elemental Te.

TABLE I. Position of emission lines.

		Present	Haglund
	A	2.5104 ±0.0001 Å 4938.8 ±0.2 eV	
($L\gamma_4$)	B	2.51228 ±0.00010 Å 4935.00 ±0.21 eV	2.5113 Å 4936.9 eV
	C	2.5310 ±0.0002 Å 4898.5 ±0.4 eV	

The target preparation and the x-ray anode power for the three Te $L\gamma_4$ measurements are listed in Table II. In all three cases the Te targets were exposed to the atmosphere before mounting in vacuum. When the x-ray tube in the present case was disassembled after the Te L_1 measurement, tellurium was found on all the relatively cool internal surfaces within a range of about 5 cm from the target area. Thus, the Te target can be considered to be continually refreshed by evaporation of the surface material. Although the Te $L\gamma_4$ spectrum was scanned three times over a period of 3 days, no changes in the profile or intensities were noted. Recall that the x-rays measured emerged along the target's normal. This geometry not only reduces the amount of self-absorption, but also reduces the contribution of fluorescent radiation from atoms outside the target area. The measurements by Haglund[7] and Noreland and Ekstig[9] were both made of the x rays that emerged from anodes at a glancing angle. In the series of measurements by Noreland and Ekstig, the anode glancing angles used were 5° and 8°. At present, I believe that the $L\gamma_4$ profile in Fig. 1 is a more reliable representation of elemental tellurium than previous recordings because of the more favorable target geometry and better counting statistics. However, the need for independent characterization of the target material is recognized.

TABLE II. Comparison of targets and spectral excitation.

	Target preparation	X-ray tube operating condition
Haglund (Ref. 7)	Powered Te rubbed onto Cu anode	~10 kV, 20–30 mA
Noreland & Ekstig (Ref. 9)	Evaporated Te on Cu anode	15 kV, 20 mA
Present	Rubbed single Te crystal on Cu anode	11 kV, 85 mA

IV. DISCUSSION

Tellurium has a stable trigonal crystalline phase at room temperature. Under other conditions it has an amorphous solid phase. In the crystalline phase, the Te atoms are joined into helical chains which extend parallel to the c axis. Each Te atom is covalently bonded to its two immediate neighbors, and the helical chains are held together by Van der Waals forces and some covalentlike bonding. **The six valence electrons are distributed into three bands, the atomic s-like ($5s^2$) states, the p-like bonding ($5p^2$) states, and the p-like nonbonding or lone-pair states, with the s-like states separated by about 8 eV from the next p-like bonding states.**

The electronic structure of Te has been most recently studied by Joannopoulos *et al.*[4] using the empirical pseudopotential method, charge-density calculations, and simple tight-binding models. In their calculations, they hybridized the bonding and antibonding p-like states with small amounts of s and d admixtures, but did not hybridize the nonbonding p-like states. A comparison of their calculated density of states showed excellent agreement with recent photoemission experiments.[5] The structure consisted of three peaks with binding energies of 1.13, 4.0, and 11.5 eV for the nonbonding (p-like), bonding (p-like), and the broader s-like states, respectively. The amplitude of the 1.13-eV peak (nonbonding) is about 1.5 times greater than the 4.0-eV peak.

The $L\gamma_4$ ($L_1O_{2,3}$) spectrum is expected to reflect the distribution of the 5p valence electrons. The measured $L\gamma_4$ spectrum in Fig. 1 is decomposed into two lines, A and B, separated by 3.6 eV. The intensity of the A component, which would correspond to a transition from the nonbonding p-like state is about $\frac{1}{3}$ the intensity of B. *Thus the* Te *$L\gamma_4$ spectrum is not in correspondence with the calculated density of states*[4] *or the photoemission spectrum.*[5]

The difference in profile between the x-ray emission and photoemission spectrum is suggested to arise from the quasiatomic character of the x-ray emission which reflects the localized charge density of the valence electrons. The photoemission spectrum, on the other hand, corresponds very well with the total density of states of the solid. The origin for the profile difference is suggested by a plot of the calculated electronic charge distribution in the energy region of the bonding and nonbonding p-like states by Joannopoulos *et al.*[4] The charge distribution of the bonding states is concentrated between the Te atoms as expected, while the distribution for the nonbonding states is more dispersed. The calculated hybridization in the p-like regions amounted to (5–10)% s and (1–5)% d admixtures, which are relatively small. The absence of any appreciable intensity in the 4930-eV energy region of Fig. 1 attests to the minimal p admixture in the s-like part of the valence band.

An estimate of the level width of the L_1 initial-state vacancy of 1.2 eV is obtained by subtracting the average bandwidth,[5] 2.2 eV, of the final state in the p-like valence bands and the instrumental width, 0.42 eV, from the FWHM of 3.8 eV for either A or B component. A recent compilation[17] gives a semiempirical total L_1 level width of about 3.3 eV. The comparative difference of 2.0 eV and the relatively narrow L_1 level width estimate of 1.2 eV is attributed to the quasiatomic character of these x-ray emission transitions, where the final state bandwidths are narrower than recorded by *XPS*. It would be very helpful to have an independent measurement of the L_1 level width.

The L_1 absorption spectrum of $_{52}$Te film measured by Nordfors and Noreland[18] has a peak of 4940.9 eV with a FWHM of 3.5 eV occurring near the onset of the L_1 absorption. The 4940.9-eV peak is thought to be the transition of the 2s electron to the unoccupied antibonding p-like states in the conduction band. X-ray photoelectron measurements[19] locate the L_1 binding energy 4939.3 ± 0.3 eV below the Fermi edge. Assuming the Fermi edge is in the middle of the 0.33 eV band gap,[1] then the conduction band should start at about 4939.6 ± 0.3 eV above the L_1 level. This estimate for the location of the conduction-band minimum is in agreement with the measured L_1 absorption which contains the level lifetime and instrumental broadening and with the interpretation of the $N_{4,5}$ absorption[20] of Te.

The spectrum in Fig. 1 also contains a small peak labeled C centered at 4898.9 ± 0.4 eV. Attempts to attribute the peak C to a transition in higher order from an impurity were unsuccessful. Therefore the peak C is tentatively identified as due to the quadrupole transition $L_1N_{4,5}$ ($2s \rightarrow 4d_{3/2,5/2}$). This identification is suggested by the estimated energy of the $L_1N_{4,5}$ transitions from the binding energies tabulated by Lotz,[21] L_1N_4 at 4897 eV and L_1N_5 at 4899 eV, and by Bearden,[8] $L_1N_{4,5}$ at 4899.9 eV. To my knowledge, this line has not been observed before.

V. CONCLUSION

Te x-ray emission in the $L\gamma_4$ spectral region has been measured with a double-crystal monochromator using direct electron bombardment excitation. The recorded $L\gamma_4$ profile was found to differ from previous measurements but to be consistent with recent band calculations and photoemission experiments. Differences between calculations and photoemission spectrum and the $L\gamma_4$ profile are attributed to a quasiatomic character of the x-ray emission process. That is, the radiative decay of the inner-shell vacancy probes the localized density of states and not the total density of states. Although the noted differences may be due to the covalent character of $_{52}$Te, it emphasizes the questionability of obtaining total density of states from x-ray emission spectra.

An emission line at 4898.9 ± 0.4 eV has been tentatively identified as the quadrupole transition Te($L_1N_{4,5}$).

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[1] J. Stuke, in *The Physics of Selenium and Tellurium*, edited by W. C. Cooper (Pergamon, London, 1969), p. 3.

[2] I. Chen, Phys. Rev. B 2, 1053 (1970); 7, 3672 (1973).

[3] M. Schlüter, J. D. Joannopoulos, M. L. Cohen, L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, Solid State Commun. 15, 1007 (1974); M. Schlüter, J. D. Joannopoulos, and M. L. Chen, Phys. Rev. Lett. 33, 89 (1974); J. D. Joannopoulos and M. Kastner, Solid State Commun. 17, 221 (1975).

[4] J. D. Joannopoulos, M. Schlüter, and M. L. Cohen, Phys. Rev. B 11, 2186 (1975).

[5] R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. 29, 274 (1972); N. J. Shevchik, M. Cardona, and T. Tejeda, Phys. Rev. B 8, 2833 (1973); T. Ichikawa, J. Phys. Soc. Jpn. 36, 1213 (1974).

[6] D. Coster, Philos. Mag. 43, 1070 (1922).

[7] P. Haglund, Ark. Mat. Astron. Fys. 28A, 8 (1941).

[8] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

[9] E. Noreland and B. Ekstig, Ark. Fys. 26, 161 (1964).

[10] R. D. Deslattes and B. Simson, Rev. Sci. Instrum. 37, 753 (1966).

[11] R. D. Deslattes, Rev. Sci. Instrum. 38, 616 (1967).

[12] R. D. Deslattes, Phys. Rev. 186, 1 (1969).

[13] R. D. Deslattes, A. Henins, R. M. Schoonover, C. L. Carroll, and H. A. Bowman, Phys. Rev. Lett. 36, 898 (1976).

[14] J. A. Bearden, A. Henins, J. G. Marzolf, W. C. Sauder, and J. S. Thomsen, Phys. Rev. 135, A899 (1964).

[15] E. Noreland, Ark. Fys. 26, 341 (1964).

[16] W. H. McMaster, N. Kerr Del Grande, J. H. Mallett, and J. H. Hubbell, "Compilation of X-ray Cross Sections," UCRL-50174-Sec. II Rev. 1 (1969).

[17] M. O. Krause, At. Data Nucl. Data Tables (to be published).

[18] B. Nordfors and E. Noreland, Ark. Fys. 20, 1 (1961). The peak position and breadth were read off the published figure and can be in error by a few tenths of an eV.

[19] P. Bergvall, O. Hörnfeldt, and C. Nordling, Ark. Fys. 17, 113 (1960).

[20] B. Sonntag, T. Tuoni, and G. Zimmerer, Phys. Status Solidi 58, 101 (1973).

[21] W. Lotz, J. Opt. Soc. Am. 60, 206 (1970).