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SOLID-STATE EFFECTS ON PIONIC ATOM X-RAY SPECTRA\*

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May 1969

Solid-state or chemical effects were observed on the intensities of lines in pionic atom x-ray spectra of several compounds and mixtures. A possible explanation of the deviations from the Z law is discussed.

Solid-state or chemical effects have been observed in muonic atoms [1-4] and recently in pionic atoms [5] by looking at the x-ray intensities of transition lines in a spectrum. Line intensities of an element are generally different, according to whether the element under consideration is pure or a part of a compound; in particular the ratios of line intensities are different [2-5]. Apart from this result, it is known that the so called Fermi-Teller Z law [6] (the prediction of capture on the constituents of a compound in proportion to their atomic number) is valid only as a general and approximate rule; the nature of the chemical bond appears to be a factor influencing the atomic capture ratio [1].

It seemed interesting to us to use the favorable  $\pi^-$  intensity available at the Berkeley 184-inch cyclotron to further study such effects. The use of  $\pi^-$  rather than  $\mu^-$ , apart from the superior intensity, has some drawbacks. The nuclear capture perturbs the lower transitions to a point where the 2p-1s, 3d-2p, and, in high-Z nuclei even 4f-3d, x-ray transitions are difficult to observe or cannot be measured. Furthermore, the nuclear capture  $\gamma$  rays cannot be distinguished from the genuine x rays by a delayed coincidence measurement, as with  $\mu^-$ . However, for high enough orbits--in particular

where the atomic capture takes place--the behavior should be the same for  $\pi^-$  and  $\mu^-$ , again apart from the nuclear capture, which may affect noncircular low- $l$  orbits for pions (3s, for example).

We used the conventional method of producing and identifying stopped  $\pi^-$ . The x rays were detected and their energy measured by means of a 1.0-cm-thick by 3.0-cm-diameter Ge(Li) detector. The detector was about 15 cm from the target and surrounded by a lead shielding. The energy resolution was 1.3 keV FWHM for the  $^{57}\text{Co}$  122-keV line. The targets were usually disks of 7.5 cm diameter and 1.25 to 2.0 cm thick ( $1.5\text{--}3.5\text{ g/cm}^2$ ). A fast coincidence ( $\approx 100$  nsec) was required between the stopped pion signal and the fast output of the Ge amplifier system [7]. The coincident pulse-height spectrum from the slow Ge amplifier output was recorded on a pulse-height analyzer. The fast coincidence was shown to cause no loss of good events above 50 keV while appreciably reducing the background due to chance coincidences. Typical instantaneous rates for the 60% duty cycle of the stretched cyclotron beam were  $10^5\text{ sec}^{-1}$  for the stopped  $\pi^-$  and  $3.5 \times 10^3\text{ sec}^{-1}$  on the Ge detector (above a 30-keV threshold).

The spectra were scanned and the peak areas evaluated after background subtraction. Two methods for evaluation were used and cross-checked. The first was a hand-and-eye method and the second an on-line computer fitting procedure. The data were corrected for the self-absorption of the x rays in the target and for the efficiency of the detector. The efficiency curve as a function of energy was carefully measured with sets of calibrated sources [8] and by use of the known relative intensities of the lines of  $^{75}\text{Se}$  and  $^{177\text{m}}\text{Lu}$  sources. An x-ray spectrum was measured not only for a particular compound but also for the corresponding mixture (when available)

of the same atomic ratio. Figure 1 shows examples of x-ray spectra for a compound and a mixture.

The results are displayed in the table. Several types of line intensity ratios have been calculated. The ratios are either for lines associated with the same element, or for pairs of lines (one from each element) in a compound or mixture. The errors include the contributions due to the background subtraction and to the uncertainties with which the detector efficiency and the target attenuation factor could be known. When a ratio of ratios is calculated for a compound and mixture pair, the uncertainties on the efficiency and the attenuation factors cancel or are reduced. In every case in which it was necessary a correction was made to take into account the difference in the yield (number of x rays of a particular transition per stopped pion) of the elements because of nuclear capture of the pions. It was difficult to determine an absolute yield with an overall uncertainty smaller than  $\pm 10\%$ , because of difficulty in evaluation of the true number of stopped  $\pi^-$ ; but the relative yields are known better, to  $\pm 5\%$ . These yields were measured by using the elements as targets whenever possible.

Before discussing the results, we wish to emphasize that the ratio of capture on the two constituents of a compound can be only indirectly deduced from a measurement of two x-ray line intensities. The intensity covers two effects: one, the initial atomic capture itself, the other, the subsequent process of the cascade. Several measurements [2-5] as well as ours have shown that the cascade is not the same for a pure element and for that element in a compound. This remarkable fact probably reflects two influences, one, the initial capture's taking place on common levels, and, two, the cascade's being dependent on the symmetry of the potential (i. e., the  $\Delta l = \pm 1$  selection

rule for radiative transitions applies only to spherical symmetry and not to the nonspherical symmetry of the potential for some compounds).

What could be noticed at first is that the line ratio of the two elements of a compound usually differed from the line ratio in the corresponding mixture. However, a compound and the corresponding mixture should not be compared directly, because the mixture was not on the atomic level. The grain size for all constituents of the mixtures was smaller than 100 mesh (0.149 mm) except for Te, which was 65 mesh (0.210 mm), and they were all larger than about 325 mesh (0.044 mm). In a first approximation for these real mixtures, the ratio  $V_1/V_2$  of the volumes of the constituents of the mixture, as well as the ratio of the rates of energy loss ( $dE/dx$ ), is effective in the capture ratio. Using the known density of the elements in the mixtures and assuming that the ratio of the rates of energy loss is proportional to  $Z_1/Z_2$ , one obtains the capture ratio proportional to  $V_1 Z_1/V_2 Z_2$ , and one can roughly explain the measured ratios for the mixtures.

A second effect is that of the binding on the intensity ratios for each element of a compound. This supports the previous observations done with  $\mu^-$ , in particular for Ti/TiO [2-4] and C/CH<sub>2</sub> [4]. The effect, if any, for Ti is much smaller in our case, in agreement with ref. 5. The effect for C is in agreement with the previous  $\mu^-$  results; it is large and opposite to that for Ti, and probably from the H to C transfer of mesons. Transitions between circular orbits ( $l = n - 1$ ) appear to be slightly favored in the compounds (see, for example, Ti/TiO<sub>2</sub>, CdTe/Cd+Te, InSb/In+Sb).

If we attempt to compare our capture ratios with a Z-law prediction [6], we see that a Z law is valid only as a rough rule.

As noticed previously with  $\mu^-$  for oxides [1], there seems to be an appreciable modulation of the Z law.

Au-Yang and Cohen have studied this problem [9] and shown that the capture takes place on high common molecular orbits and that solid-state effects cannot be neglected. They have performed numerical calculations for a few cases, in particular for ZnS, for which they expect a ratio of 3.0, which compares well with our experiment. In agreement with these authors, we find that the atomic capture is influenced by the Z ratio, the ratio of the radii of the two types of ions or atoms, and the effective charge parameter  $Z_f$ . The effective charge parameter is an estimate of the charge transfer; it characterizes the chemical bond and is defined as the amount of ionic character times the number of valence electrons. The ionic character of a bond is related to the difference in electronegativity of the atoms; these parameters are from Pauling [10]. For  $Z_1/Z_2 \leq 1$ ,  $Z_f$  might be the most important factor, as in ZnSe, where the deviation from the Z law is large. But the additional effect of  $Z_f$ , in favor of the positive ion, is perhaps small when  $Z_1/Z_2 > 1$ ; it can also be counterbalanced by the effect of the ratio of the radii, usually smaller than 1, favoring the negative ion. The comparison of FeS with FeS<sub>2</sub> is direct evidence for the effect of  $Z_f$ .

The KCl and CaCl<sub>2</sub> compared as solutions in water and as the anhydrous salts, also show the effect of  $Z_f$ , but with the complication brought by the dissociation. Concerning the Cu<sub>3</sub>Au alloy, from the most reliable ratio, 4f-3d Cu/7i-6h Au, one might conclude that the potential of the unordered sample is more like that of the mixture 3 Cu+Au. The ordered sample was characterized by a factor-of-2 increase in the electrical conductivity after the thermal ordering process.



Beside studying isotope effects on the shifts and widths [11] with  $^{44}\text{CaCl}_2$  and  $^{40}\text{CaCl}_2$  targets (our results [11] show smaller line shift and width in  $^{44}\text{Ca}$  than for  $^{40}\text{Ca}$ ), we searched for a possible nuclear-mass lattice-recoil effect on the atomic capture ratio, following a suggestion by E. Teller. Our results might show an effect ( $\approx 5\%$ ), seen in three different ratios, but the uncertainties are as large as the effect. Again, apart from the intensity, a study with  $\mu^-$  would be preferable.

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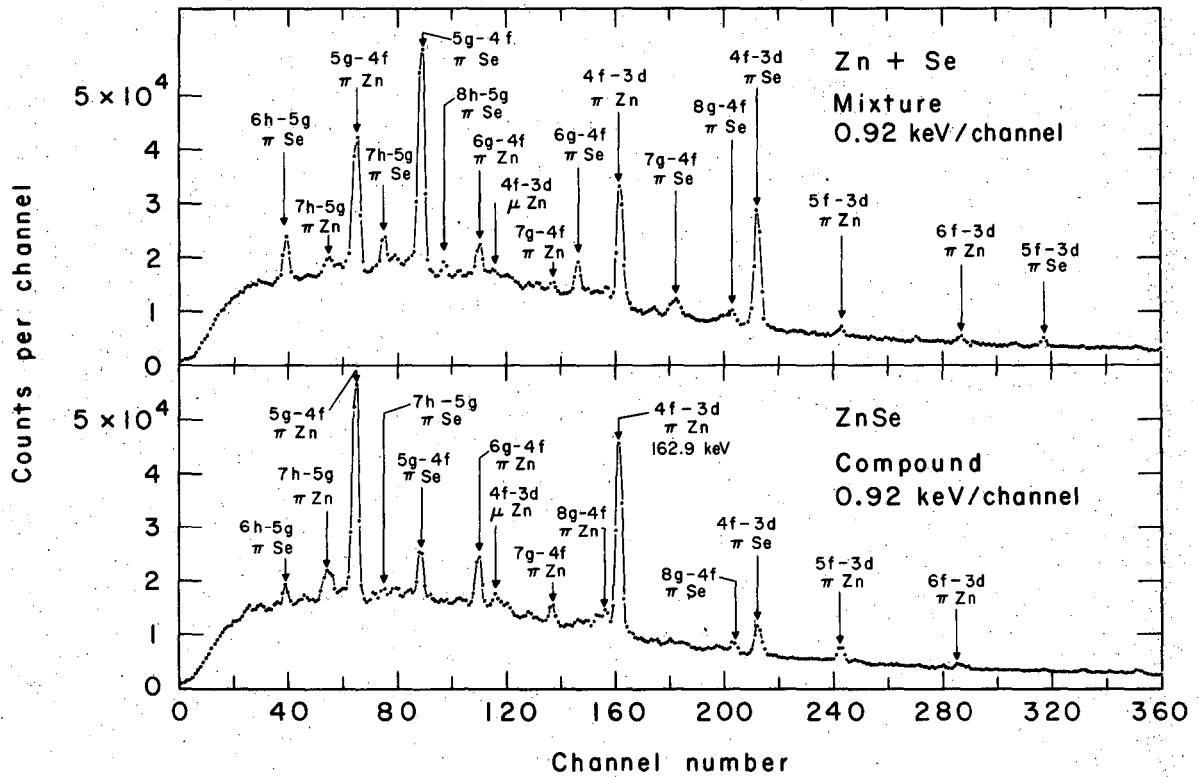
#### FOOTNOTES AND REFERENCES

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Fig. 1. Pionic atom X-ray spectrum of a compound and a mixture.

Table I. Experimental results

All of the quoted ratios are given for a one-to-one compound. The ratios given on the same lines as element yields include the effect of the latter.

Samples	$Z_1/Z_2$	$Z_f^a$	Line ratio <sup>b</sup>	In first sample	In second sample	First line yield <sup>c</sup>	Second line yield <sup>d</sup>	Ratio of ratios <sup>e</sup>
ZnS, Zn+S	1.87	0.36	4f-3d Zn/3d-2p S	2.68 ±0.12	1.42 ±0.06			1.89 ±0.08
			5f-3d Zn/4f-3d Zn	2.54 ±0.31	1.35 ±0.17	0.40 ±0.05	0.38 ±0.04	1.23 ±0.08
			6g-4f Zn/5g-4f Zn	0.16 ±0.01	0.130±0.007			0.82 ±0.04
			4d-2p S/3d-2p S	0.180±0.015	0.22 ±0.02			0.83 ±0.09
ZnSe, Zn+Se	0.89	0.30	4f-3d Zn/4f-3d Se	3.57 ±0.19	0.64 ±0.04			5.58 ±0.34
			5f-3d Zn/4f-3d Zn	4.10 ±0.49	0.74 ±0.09	0.40 ±0.05	0.46 ±0.04	1.17 ±0.12
			6g-4f Zn/5g-4f Zn	0.14 ±0.01	0.12 ±0.01			0.78 ±0.07
FeS, Fe+S	1.62	0.24	4f-3d Fe/3d-2p S	1.67 ±0.10	0.74 ±0.04			2.26 ±0.11
			2.75 ±0.31	1.22 ±0.13	0.23 ±0.02	0.38 ±0.04		
FeS <sub>2</sub> , Fe+2S	1.62	0.12	4f-3d Fe/3d-2p S	1.30 ±0.08	0.85 ±0.05			1.53 ±0.10
CdTe, Cd+Te	0.92	0.08	5g-4f Cd/5g-4f Te	0.84 ±0.05	0.77 ±0.05	0.40 ±0.04	0.43 ±0.04	1.09 ±0.07
			6h-5g Cd/6h-5g Te	0.90 ±0.10	0.82 ±0.09			1.15 ±0.10
			0.83 ±0.08	0.72 ±0.07				
			0.85 ±0.11	0.74 ±0.10	0.44 ±0.04	0.45 ±0.04		
			7h-5g Cd/6h-5g Cd	0.230±0.025	0.25 ±0.03			0.92 ±0.11
InSb, In+Sb	0.96	0.03	7h-5g Te/6h-5g Te	0.155±0.02	0.18 ±0.02			0.86 ±0.13
			7i-6h Te/6h-5g Te	1.18 ±0.12	0.85 ±0.10			1.39 ±0.16
			5g-4f In/5g-4f Sb	1.02 ±0.05	0.99 ±0.05			1.03 ±0.05
			1.07 ±0.11	1.04 ±0.10	0.43 ±0.04	0.45 ±0.04		
			0.94 ±0.09	0.91 ±0.09			1.03 ±0.09	
Ti, TiO <sub>2</sub>			7h-5g In/6h-5g In	0.94 ±0.12	0.91 ±0.12	0.47 ±0.04	0.47 ±0.04	
			7h-5g Sb/6h-5g Sb	0.195±0.025	0.23 ±0.03			0.85 ±0.13
			0.21 ±0.02	0.225±0.030			0.93 ±0.14	
			5f-3d Ti/4f-3d Ti	0.208±0.018	0.200±0.018			1.04 ±0.08
			6f-3d Ti/4f-3d Ti	0.214±0.020	0.207±0.020			1.04 ±0.09
			7f-3d Ti/4f-3d Ti	0.049±0.006	0.059±0.008			0.84 ±0.14
			7g-4f Ti/4f-3d Ti	0.157±0.019	0.147±0.018			1.07 ±0.12
			4f-3d Ti/3d-2p Ti	1.59 ±0.14	1.59 ±0.15	0.295±0.03	0.195±0.02	1.00 ±0.14
C, CH <sub>2</sub>			4f-3d Ti/3d-2p Ti	1.05 ±0.14	1.05 ±0.15			
			3p-1s C/2p-1s C	0.24 ±0.03	0.29 ±0.04			0.71 ±0.11
			4p-1s C/2p-1s C	0.135±0.025	0.215±0.03			0.63 ±0.12
CaCl <sub>2</sub> , CaCl <sub>2</sub> (H <sub>2</sub> O)	1.18	0.62	5p-1s C/2p-1s C	0.11 ±0.02	0.245±0.035			0.45 ±0.09
			3d-2p Ca/3d-2p Cl	0.775±0.040	0.82 ±0.05	0.24 ±0.02	0.355±0.03	0.95 ±0.06
			1.15 ±0.12	1.22 ±0.12				
			5f-3d Ca/3d-2p Cl	1.44 ±0.12	1.40 ±0.23			1.03 ±0.17
KCl, KCl(H <sub>2</sub> O)	1.12	0.70	6f-3d Ca/5f-3d Ca	0.46 ±0.05	0.35 ±0.12			1.30 ±0.45
			4d-2p Cl/3d-2p Cl	0.09 ±0.01	0.12 ±0.02			0.74 ±0.14
			3d-2p K/3d-2p Cl	0.99 ±0.04	0.71 ±0.05	0.31 ±0.03	0.355±0.03	1.39 ±0.10
			1.13 ±0.11	0.81 ±0.94				
CsCl	3.23	0.73	4f-3d K/3d-2p Cl	1.15 ±0.07	0.91 ±0.07	0.31 ±0.03	0.355±0.03	1.27 ±0.07
			1.32 ±0.13	1.04 ±0.12				
			5g-4f Cs/3d-2p Cl	2.33 ±0.11	1.84 ±0.20	0.45 ±0.05	0.355±0.03	
			1.84 ±0.20	2.02 ±0.10				
<sup>44</sup> CaCl <sub>2</sub> , <sup>40</sup> CaCl <sub>2</sub>			6h-5g Cs/3d-2p Cl	2.02 ±0.10	1.63 ±0.16	0.44 ±0.04	0.355±0.03	
			7h-5g Cs/6h-5g Cs	0.19 ±0.02	0.19 ±0.02			
			3d-2p Ca/3d-2p Cl	0.835±0.055	0.89 ±0.06			0.94 ±0.08
			1.25 ±0.13	1.31 ±0.14	0.24 ±0.02	0.355±0.03		
			6f-3d Ca/6f-3d Cl	2.01 ±0.22	2.15 ±0.22			0.94 ±0.10
Cu <sub>2</sub> Au(ordered), 0.37 Cu <sub>3</sub> Au(unordered)			4d-2p Cl/3d-2p Cl	0.115±0.010	0.125±0.010			0.93 ±0.10
			4f-3d Ca/3d-2p Cl	0.895±0.080	0.945±0.080			0.95 ±0.08
			1.11 ±0.14	1.18 ±0.15	0.285±0.025	0.355±0.03		
3Cu+Au			4f-3d Cu/7i-6h Au	0.407±0.022	0.427±0.023	0.31 ±0.03	0.46 ±0.03	0.95 ±0.05
			0.670±0.065	0.702±0.068				
3Cu+Au			4f-3d Cu/7i-6h Au	0.442±0.027	0.726±0.074	0.31 ±0.03	0.46 ±0.03	
			0.726±0.074					

a. Effective charge parameter, defined in text.

b. The ratio of the intensity of the two listed transition lines.

c. Transition line yield in the first element of column 4 defined as number of X-rays per stopped pion.

d. Transition line yield in the second element of column 4 defined as number of X-rays per stopped pion.

e. Ratio of the intensity ratios of columns 5 and 6.

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