Letters to the Editor

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The Soft X-Ray Valence Band Spectra and the Heat of Formation of Chemical Compounds and Alloys

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March 31, 1950

The soft x-ray K-valence emission spectra of Mg, Al, and Si in the pure metallic state, as well as in their oxides, of silicon in SiC and L_{III}-valence emission spectra of Fe in the alloy $AlFe_3$ have been investigated with bent gypsum and mica crystals in a vacuum spectrograph. The shift of K_β- or K-valence emission band of the constituent elements A and B of the compound or alloy A_mB_n toward the longer or shorter wave-length side with respect to the respective pure elements have been qualitatively, as well as semiquantitatively correlated with the heat of formation of the corresponding compound or alloy. The large values of the heat of formation for most of the compounds and the negligibly small values for the alloys and the homopolar compound like SiC, etc., cannot be explained from the consideration of the changes in the values of the specific heats of the constituent elements when forming a compound or alloy.

In the equation:

$$\underset{\leftarrow Q_A\rightarrow}{m\cdot V_A\cdot\Delta E_A}\pm\underset{\leftarrow Q_B\rightarrow}{n\cdot V_B\cdot\Delta E_B}=Q/23.02,$$

where V_A and V_B are the numbers of electrons in the outermost level of the elements A and B, respectively, involved in emission of the valence band spectra, e.g. 2 for Mg, 3 for Al, 4 for Si, 6 for oxygen, 8 for Fe, etc.; ΔE_A and ΔE_B are the shifts in electron volts of the valence band peak of elements A and B in the compound A_mB_n with respect to the respective pure elements A and B; Q is the heat of formation of the compound or alloy expressed in kilocalories per gram-formula weight and 23.02 is the conversion factor.

If in the equation ΔE_A and ΔE_B are individually zero or negligible, $Q=0$, or is negligibly small. If ΔE_A and ΔE_B are oppositely directed, the value of Q may be large or small or even negative (endothermic) according to the relative values of ΔE_A and ΔE_B. The data are given in Table I.

Table I. Soft x-ray valence band shifts and the heat of formation of the compounds and alloys.

Specimens A_mB_n	ΔE_A (ev)	Q_A (kcal.)	ΔE_B (ev)	Q_B (kcal.)	$Q_{A_mB_n}$	$Q_{A_mB_n}$ (thermochemical data)
MgO	4.5	207	0.52	72	135	145
Al_2O_3	4.48	618	0.52	215	403	400
SiO_2	3.9	359	0.52	144	215	200
MgS	(expected 5)	*237*	1.12	155	···	82
$AlFe_3$	2.0	138	0.24	132	6	(of the order of 10)
SiC	(no shift for Si)	0	(no shift for C)	0	0	(of the order of 1)

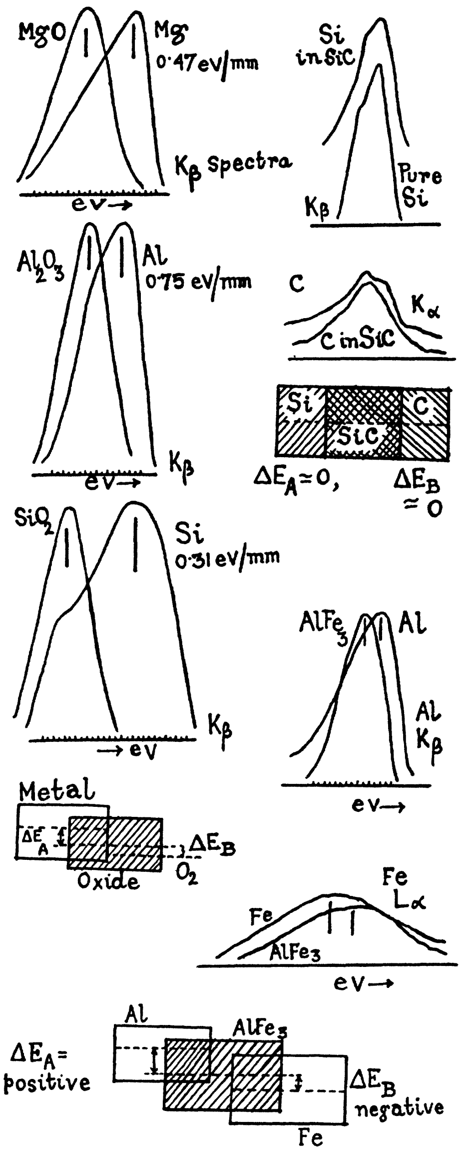

Fig. 1. Tracings of the original microphotometer records of the valence band spectra of elements in pure solid state, in compounds and in alloys.

The constant value of the shift 0.52 ev in the case of oxygen for which V_B is taken to be six is justified from the appearance in the same position of the peak of oxygen K_α-band for all these oxides taken by O'Bryan and Skinner.[1] For a shift towards the longer wave-length ΔE is positive, which is to be connected with the heat of evolution, and for a shift towards the shorter wave-length ΔE is to be counted as negative, which is to be connected with the heat of absorption.

The equation, although inadequate to give an exact value of the heat of formation, has been tested for a large number of compounds and alloys and found to indicate correctly the direction of the shift of valence band spectra of the constituent elements with respect to the spectra for the pure elements. Approximate calculation shows that the contribution of the specific heat factor is very small.

The uncertainties in the application of the equation are due to the following factors:

(1) The intensity distribution of the valence band spectra of the

elements changes considerably when in compounds. So the values of ΔE_A and ΔE_B measured as the distance between the two peaks of the valence bands may not be accurate.

(2) The appearance of structures in the valence band spectra create much difficulty in ascertaining the correct values for ΔE_A and ΔE_B.

(3) If one of the constituents is ordinarily a gas, usually a position for the gaseous state is determined from the formula, knowing the value of the heat of formation of the particular compound. Once this has been done, the values of ΔE for other compounds involving the particular gas are determined with respect to the calculated position.

Although there are so many limitations, the equation helps to identify and explain the origin of particular bands in soft x-ray spectra, to indicate the direction and the amount of shift for the elements in compounds and alloy, and to suggest a straightforward picture as the mechanism of the evolution or absorption of heat in a chemical reaction.

I wish to express my sincere thanks to Professor S. N. Bose, Head of the Department of Physics, University College of Science, Calcutta, who has given me the facilities of work in his laboratory and encouraged me during the progress of the work. My thanks are also due to the National Institute of Sciences of India for appointing me a Research Fellow of the Institute.

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[1] O'Bryan and Skinner, Proc. Roy. Soc. **A176**, 229 (1940).

The Gamma-Ray Spectrum from the Absorption of π^--Mesons in Deuterium*

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August 25, 1950

The gamma-ray spectrum resulting from the absorption of π^--mesons in deuterium has been analyzed with a pair spectrometer having 30 channels covering a range of 3 to 1 in energy. The experimental arrangement is similar to that discussed in previous letters by the same authors.[1,2] The deuterium is contained in the pressure vessel at 2700 p.s.i. at the temperature of liquid nitrogen. Its density[3] is 0.096 as compared with a hydrogen density of 0.046 under the same conditions.

Ten runs were made over a 72-hour period without changing the physical set-up. The regions centering on 130 Mev and 70 Mev were examined with full sensitivity. Comparisons were obtained between hydrogen, deuterium, helium, and vacuum background in the upper energy region. In the lower energy region deuterium, helium, and background were examined so that a limit might be set to the null effect observed there in deuterium.

The spectrum from π^--capture in hydrogen has been attributed to the reactions

(a) $\pi^-+p\rightarrow n+\gamma$ ($E_\gamma=131$ Mev).
(b) $\pi^-+p\rightarrow n+\pi^0\rightarrow n+2\gamma$ ($E_\gamma=70$ Mev).

In deuterium one or more of the following reactions are probable:

(c) $\pi^-+d\rightarrow 2n+\gamma$ ($E_\gamma=0$ to 135 Mev).
(d) $\pi^-+d\rightarrow 2n+\pi^0\rightarrow 2n+2\gamma$ ($E_\gamma=70$ Mev).
(e) $\pi^-+d\rightarrow 2n$.

By combining the channels in which a positive counting rate is observed we find the following total counting rates for the various processes:

(a)	0.470±0.046 c.p.m.	For a total of 0.925±0.1 c.p.m. in hydrogen.
(b)	0.455±0.09 c.p.m.	
(c)	0.275±0.034 c.p.m.	For a total of 0.275±0.04 c.p.m. in deuterium.
(d)	−0.008±0.020 c.p.m.	

The ratio of the yield in deuterium to that in hydrogen is 0.30±0.04.

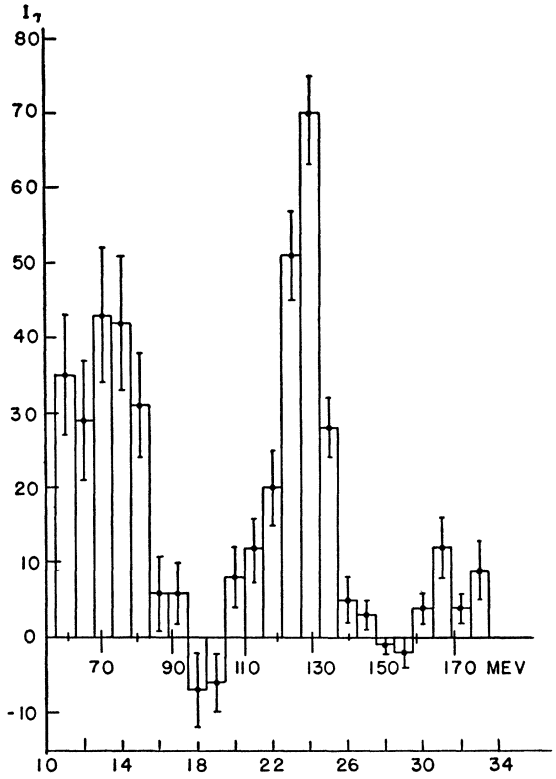

FIG. 1. Gamma-ray spectrum from absorption of π^--mesons in hydrogen. The lower numbers represent spectrometer channels.

(e) Attempts are being made to detect the fast neutrons from this process, but without conclusive results at this time. This process probably accounts for the remainder of the π^--captures in deuterium.

The runs with helium were made to see whether the background was increased by π^0-production from fast protons scattered into the deuterium, since it is known[4] that the cross section for production of π^0-mesons by protons on neutrons is much greater than for protons on protons. No counts above vacuum background

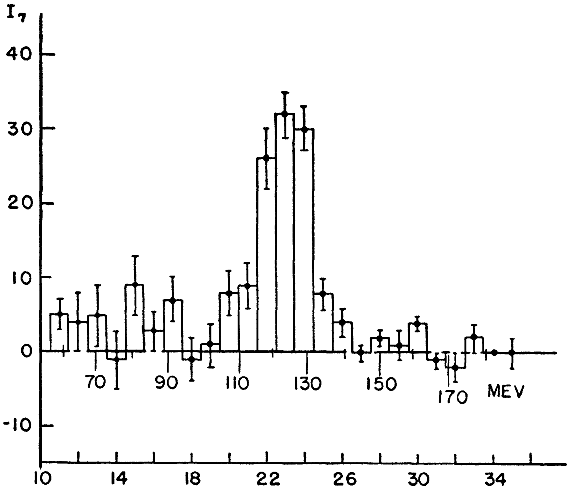

FIG. 2. Gamma-ray spectrum from absorption of π^--mesons in deuterium. Same relative scale as Fig. 1.