

### 105. Rare-earth Carbides. Part III.\* X-Ray Absorption.

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*K*-Edge absorption of some rare-earth carbides has been studied in further attempts to rationalise the structure of these compounds. The attainment of bivalent states in samarium and ytterbium carbides receives further confirmation, and from consideration of energy values the "free electron" concept appears substantiated.

POLARISING field effects upon *4f* transitions in the lanthanons have been studied through the visual absorption spectrum,<sup>1</sup> and similar perturbation effects at the *K* and *L* levels have been observed in compounds of other elements by X-ray absorption techniques.<sup>2</sup> X-Ray absorptions of the rare-earth carbides were initially studied to elucidate anomalies

TABLE I. Comparison of wavelength and energy values for *K*-absorption edges of rare-earth metals and carbides.

Element	Compound	Calc.*		Observed			
		<i>K</i> λ (Å)	<i>K</i> <sub>E</sub> (kev)	<i>K</i> λ (Å)	<i>K</i> <sub>E</sub> (kev)	Δ <i>K</i> (Å)	Δ <i>E</i> (kev)
Sc	Metal	2.751	4.496	2.795	4.435		
	Monocarbide			2.795	4.435	0.0	0.0
Y	Metal	0.726	17.037	0.725	17.103		
	Dicarbide			0.718	17.258	0.0065	0.155
La	Metal	0.318	38.931	0.318	38.982		
	Dicarbide			0.307	40.379	0.011	1.397
Ce	Metal	0.306	40.449	0.308	40.248		
	Dicarbide			0.301	41.184	0.007	0.936
Pr	Metal	0.295	41.998	0.292	42.453		
	Dicarbide			0.286	43.344	0.006	0.891
Nd	Metal	0.285	43.571	0.285	43.496		
	Dicarbide			0.280	44.273	0.005	0.777
Sm	Metal	0.264	46.846	0.263	47.135		
	Dicarbide			0.263	47.135	0.0	0.0
Gd	Metal	0.246	50.229	0.248	49.985		
	Dicarbide			0.244	50.805	0.004	0.820
Tb	Metal	0.238	51.998	0.237	52.305		
	Dicarbide			0.235	52.751	0.002	0.446
Dy	Metal	0.230	53.789	0.234	52.976		
	Dicarbide			0.231	53.664	0.003	0.688
Ho	Metal	0.222	55.615	0.219	56.605		
	Dicarbide			0.219	56.605	0.0	0.0
Er	Metal		57.483	0.214	57.927		
	Dicarbide			0.214	57.927	0.0	0.0
Yb	Metal	0.202	61.303	0.200	61.982		
	Dicarbide			0.197	62.926	0.003	0.944

\* Fine and Hendel, *Nucleonics*, 1955, **13**, No. 3, 36; Bragg and Bragg, "The Solid State," Bell, London, 1949, p. 318.

in powder-diffraction studies (Part I), but have now been more directly applied in structure determinations.

Morehouse<sup>3</sup> showed the effect of variation in valency upon the absorption coefficient

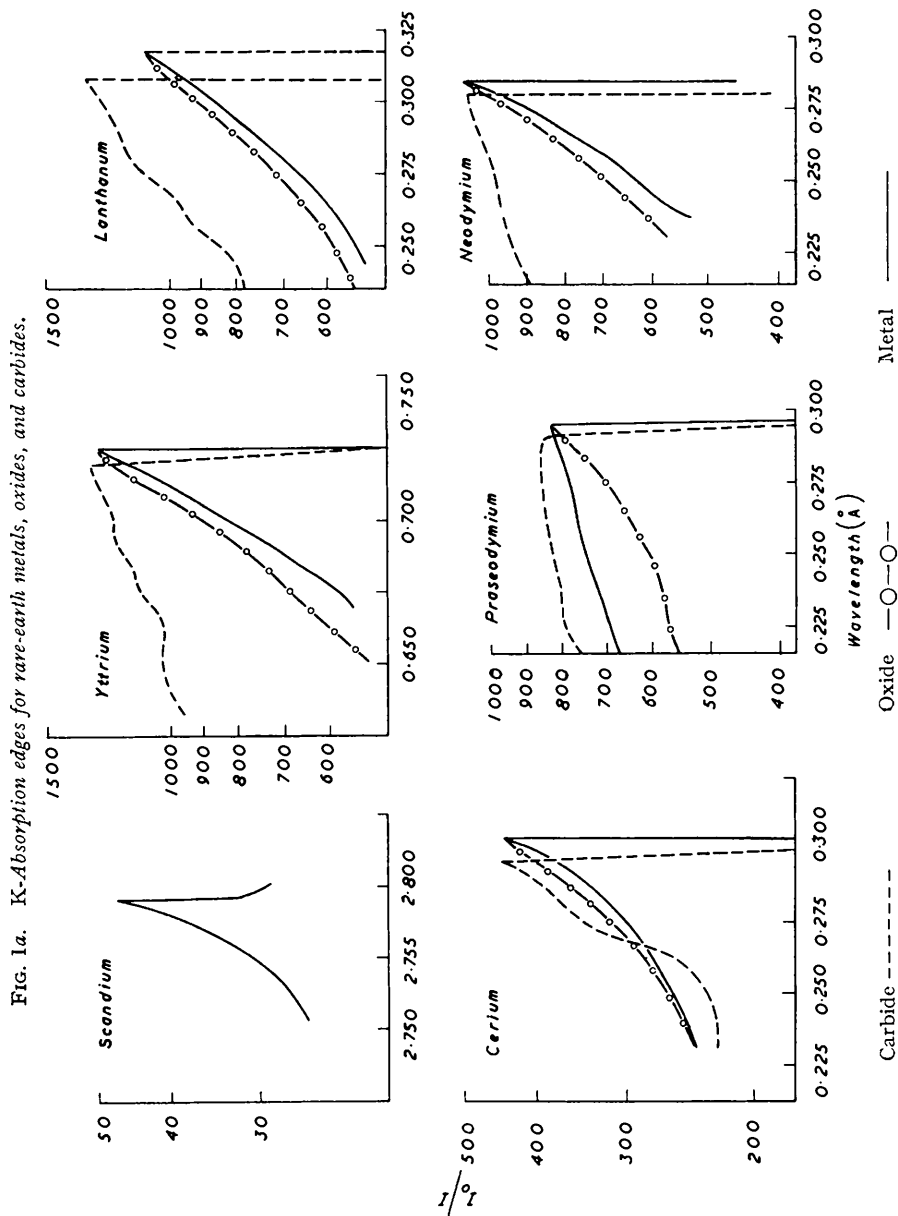
\* Parts I and II, preceding papers.

<sup>1</sup> Vickery, *J. Mol. Spectroscopy*, June, 1958; Halleck and Eckardt, *Z. Naturforsch.*, 1953, **8a**, 660; Boulanger, *Ann. Chim.*, 1952, **7**, 732.

<sup>2</sup> Cotton and Ballhausen, *J. Chem. Phys.*, 1956, **25**, 617; 1957, **26**, 1758; Kauer, *Z. phys. Chem. (Frankfurt)*, 1956, **6**, 105; Manescu, *Compt. rend.*, 1947, **225**, 537; Vainshtein, *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 1944, 382.

<sup>3</sup> Morehouse, *Phys. Rev.*, 1927, **29**, 767, 924.

for an element, and Owen and Williams<sup>4</sup> also demonstrated the effects of chemical combination upon *X*-ray absorption spectra. Such studies are of increasing frequency, and the fine structures of *K* and *L* absorption edges have permitted some assumptions to be made on the effects of association upon energy transfers at these levels.<sup>5</sup>

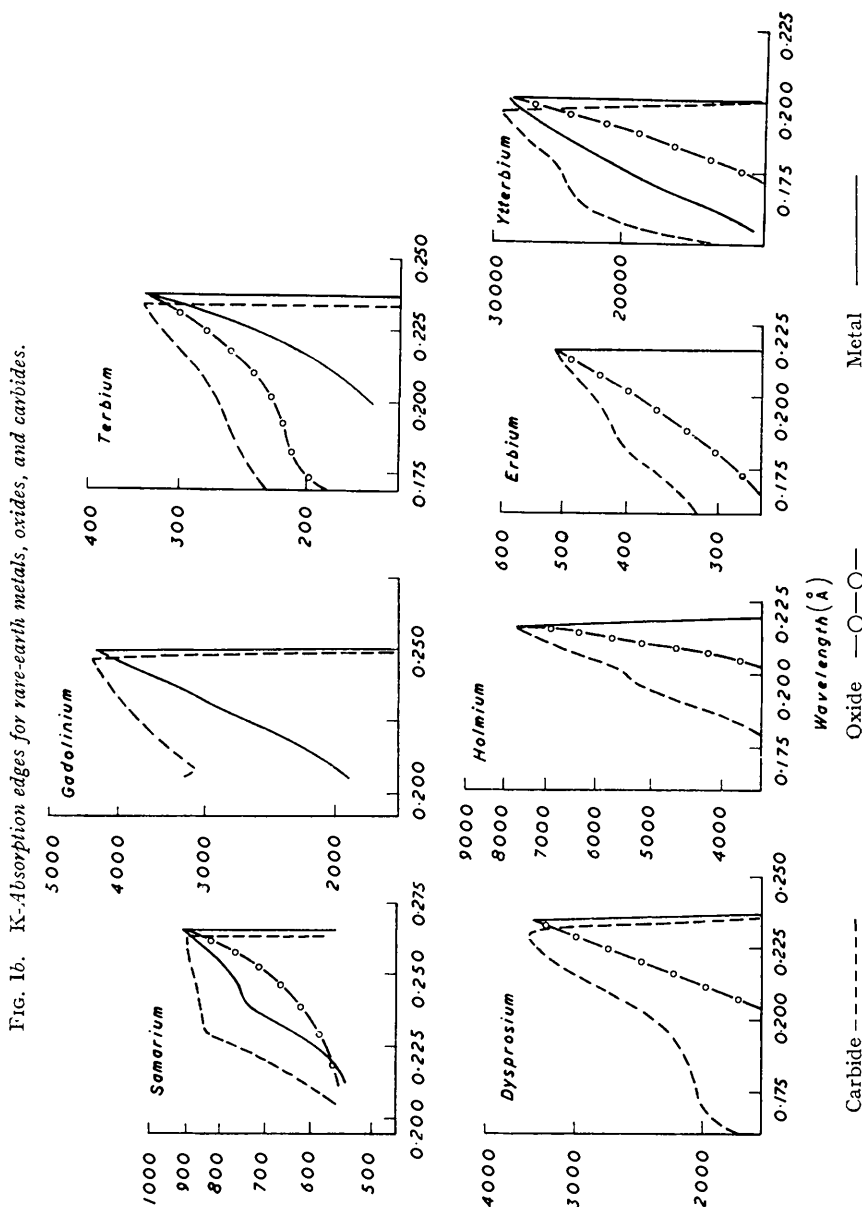


We have now examined the *X*-absorption spectra at the *K* level (up to *ca.* 3 Å) of some rare-earth carbides and, as can be seen from Figs. 1a and 1b, structures of the *K*-absorption

<sup>4</sup> Owen and Williams, *Proc. Roy. Soc.*, 1931, *A*, **132**, 282.

<sup>5</sup> Rudstrom, *Arkiv Fys.*, 1957, **12**, 259, 287; Vainshtein, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 1196; Leder, *Phys. Rev.*, 1956, **101**, 1460; Cauchois, *J. Phys. Radium*, 1952, **13**, 113; Hill, Church, and Milhelich, *Rev. Sci. Instr.*, 1952, **23**, 523.

edges differ markedly from those of the corresponding metals and oxides. Absorption-edge wavelengths now determined for the metals and carbides together with energy values and differentials are given in Table I.



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Some *L*-absorption spectra have also been superficially examined, but at this level perturbation makes interpretation too complex to be attempted. Fig. 2 compares the gadolinium carbide *L*-absorption spectrum with that of the oxide. We have not studied reflection absorption in the visible region but, from the results now obtained, one would

expect the absorption spectra between, *e.g.*, 300 and 600  $\mu$  to exhibit even grosser distortion and perturbation than hitherto observed.<sup>1</sup>

Qualitative aspects of the *K*-absorption spectra are: scandium carbide, oxide, and metal show the same pattern; that the carbide *K*-edge does not shift as in some of the other carbides is interesting since, with fewer shielding electrons, a greater perturbing effect might be expected. The small ionic size of scandium, however, leads to a higher electron density, which undoubtedly increases the overall shielding. Although the fine structure of the *K* edge for yttrium oxide differs slightly from that of the metal, the carbide absorption is widely variant at wavelengths below the *K* edge, which itself is shifted to shorter values. This edge-shift is again somewhat less than might be expected in view of the absence of shielding electrons in the 6th, 5th, and 4*f* orbitals; the shift is, however, greater than that seen in dysprosium carbides (Dy being of similar ionic radius to Y), but the energy differential is, of course, less.

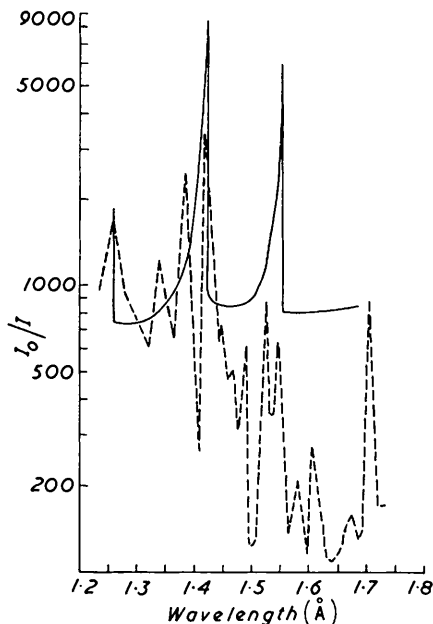


FIG. 2. *L*-Absorption spectra of  $Gd_2O_3$  (—) and  $GdC_2$  (---).

*K*-Edge shift is greatest in the absorption spectrum of lanthanum carbide, and this might be expected, since the lanthanum ion is the largest of the rare earths and possesses no shielding 4*f* electrons. The carbide fine edge shows appreciable variation from those of the oxide and the metal.

Fine structures of the *K* edges of the potentially bivalent lanthanons, samarium and ytterbium, show some similarity, absorbancy increasing in the order oxide < metal < carbide. Higher absorbancy might be expected in the bivalent than the trivalent state because of the increased electron density at lower electron levels in the former. Samarium and ytterbium metals being partially bivalent, we feel therefore the position and approximation of the fine *K* edges of samarium and ytterbium carbides to those of their metals to be further evidence that the bivalent state is adopted in them. Europium and its compounds were not studied, but may be expected to display absorption characteristics similar to those of the samarium compounds.

In conformity with the above, one would expect in higher-valency compounds the lessened electron shielding at lower orbits to effect lower absorbancies than in the lower-valency state of the same element. This relationship is generally shown in the *K* spectra of cerium, praseodymium, and terbium oxides and carbides, but the relationship of the

metal absorption curves to those of the compounds is anomalous. This anomaly is accentuated by the appearance of the cerium spectra at very low wavelengths, and the overall disposition of the cerium and terbium spectra which appears to suggest, very incongruently, that the metal has a higher valency than the oxide. In this context therefore it is clear that the relationship between the *K* absorption spectra of cerium, praseodymium, and terbium and those of their oxides and carbides is anomalous in comparison with those of the other rare earths.

That ionic size and electron density are factors in shielding the *K* shell from perturbation appears from the lack of *K*-edge shift from holmium onwards. The *K*-absorption edge for ytterbium carbide does shift, but this is attributed to the development of bivalency in this compound, giving a larger ionic radius for ytterbium and thus a lower electron density.

Absorption curves are essentially probability functions, showing variations in the probability of transitions at given energy levels, and much of the influence of bonding and atomic states is demonstrated in the edge structure, which is related to the number and nature of the nearest neighbours as well as the interatomic distances. It is not yet possible, however, to do more than deduce from these edge structures the above qualitative views.

In the Figures, the abscissæ are given in Ångström units for qualitative convenience. In Table 1 the wavelengths have been converted into energy units (kev) by using DuMond and Cohen's equation,<sup>6</sup>  $E \text{ (kev)} = 12.3964/\lambda \text{ Å}$ , and differentials are tabulated for the *K*-energy levels of the metals and carbides. Also given are *K* critical absorption-energy values listed by Fine and Hendel<sup>7</sup> for the rare-earth metals. As is seen, agreement of values now obtained and those calculated is reasonable (*ca.* 1%).

Since the energy differentials observed essentially represent the excess of energy required to transfer an inner-shell electron in the carbides to the first empty shell above that required for the same transition in the metals, it is suggested that, in the carbides, the *5d* electron is the "free electron" required by Stackelberg's theory (see Parts I and II, preceding papers) so that the liberated *K* electron has to migrate to the *6s* level before finding a suitable resting place.

Absorption coefficients at the *K* edge have been calculated through the usual equation,  $I = I_0 e^{-\mu T}$ , and are given in Table 2 for both metals and carbides. All absorption curves and absorption coefficients have been related to identical rare-earth contents.

TABLE 2. *Rare-earth metal and carbide absorption coefficients at K-absorption edge.*

Element	Compound	$I_0/I$	$\mu$	Element	Compound	$I_0/I$	$\mu$
Sc	Metal	49.5	26.01	Gd	Metal	440	40.59
	Monocarbide	49.5	26.01		Dicarbide	435	40.51
Y	Metal	1,350	48.06	Tb	Metal	352	39.10
	Dicarbide	1,348	48.05		Dicarbide	355	39.16
La	Metal	1,140	46.94	Dy	Metal ...	3,500	54.42
	Dicarbide	1,320	47.93		Dicarbide	3,500	54.42
Ce	Metal	460	40.88	Ho	Metal	8,000	59.93
	Dicarbide	470	41.03		Dicarbide	8,000	59.93
Pr	Metal	865	45.09	Er	Metal	525	41.77
	Dicarbide	860	45.06		Dicarbide	525	41.77
Nd	Metal	1,012	46.13	Yb	Metal	29,500	68.63
	Dicarbide	1,013	46.14		Dicarbide	30,000	68.74
Sm	Metal	920	45.51				
	Dicarbide	930	45.58				

In general, we consider that our data establish, with some certainty, that the structure assumed for the rare-earth dicarbides by Stackelberg<sup>8</sup> and Spedding *et al.*<sup>9</sup> is correct for all the carbides studied except for those of scandium, samarium, and ytterbium (and probably also europium). In the potentially bivalent elements it appears that the carbides

<sup>6</sup> DuMond and Cohen, *Phys. Rev.*, 1951, **82**, 555.

<sup>7</sup> Fine and Hendel, *Nucleonics*, 1955, **13**, No. 3, 36.

<sup>8</sup> Stackelberg, *Z. phys. Chem.*, 1930, **B**, **9**, 437.

<sup>9</sup> Spedding *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 1804.

closely approach ionic compounds, but if so then they should no longer be electrically conducting. The problem of their structure, therefore, still remains. Similarly, with scandium, Hume-Rothery gave evidence<sup>10</sup> that scandium carbide could be an interstitial compound, and the crystal structure (Part I) appears to confirm this, since the metal itself has a hexagonal habit, and it is unlikely that the intrusion of relatively small amounts of carbon will markedly alter this.

#### EXPERIMENTAL

The carbides were prepared as in Part I. Specimens were prepared for *X*-ray absorption studies by screening the carbides through a 100-mesh sieve under an inert solvent, replacing the solvent with ether, and evaporating the ether under vacuum. The fine carbide powders were then pressed into a filter holder so milled that the depth of penetration was approximately 1 mm. The actual depth was determined micrometrically, and the other dimensions of the aperture were accurately known. The specimen was sealed into the filter holder with acetate tape, and corrections were made for void space in the sample.

*X*-Irradiation was effected in the usual way, with a two-crystal spectrometer and Geiger recording at quarter-degree intervals, equivalent wavelengths being determined through the Bragg equation,  $n\lambda = 2d \sin \theta$ . A tungsten target tube with stabilised power supply supplied the radiation. Standard radiation (blank) and transmitted intensity were determined initially by direct counting, but later the Geiger counters were connected to a differential counter, incident radiation intensity being kept constant at  $50,000 \pm 100$  c.p.m.  $I_0/I$  values were obtained directly, and absorption coefficients determined through the appropriate formulæ. Check comparisons were made on known, pure elements as standards, and absorption curves were plotted as the mean of several—usually six—determinations at given points.

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<sup>10</sup> Hume-Rothery, *Phil. Mag.*, 1953, **44**, 1154.

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