

LETTERS TO THE EDITOR

CHEMICAL SHIFTS OF THE COBALT K
ABSORPTION DISCONTINUITY IN SOME
COMPOUNDS

CONSIDERABLE work has been reported on chemical shifts in X-ray absorption spectra. It has been recently¹⁻² shown that the Kunzl's law has a very qualitative validity for the shifts for the cations alone in the compounds and that one observes either a positive or a negative shift depending upon whether the absorbing ion is a cation or an anion. The magnitude of the chemical shift is seen to depend upon the effective ionic charge on the absorbing atom, which appears at its periphery as a result of its participation in chemical bonding. In this note we present some of the results of our X-ray spectroscopic investigations on certain binary (and also a ternary compound) compounds of cobalt.

The K absorption discontinuity of cobalt was recorded photographically in metallic cobalt and its compounds using a Cauchois type bent crystal X-ray spectrograph of diameter 40 cm with a mica crystal oriented to reflect from its (100) planes. Microphotometer records of the spectra were obtained with magnification 100 on the Spectroline Scanner made by M/s. Applied Research Laboratories, U.S.A. The compounds CoO, Co₂O₃ and CoCl₂ of AR grade, were obtained from M/s. BDH Private Limited, Bombay. The cobalt arsenides, namely CoAs, CoAs₂, CoAsS and CoAs₃ were prepared in the laboratory by heating the constituent elements in stoichiometric proportion in evacuated sealed silica ampules, following the method of Heyding *et al.*³⁻⁵. The formation of these compounds was checked by studying their powder patterns. Further details of the experimental technique are described elsewhere¹⁻².

The results of the measurements are given in Table I. As is well known⁶, the K absorption discontinuity of cobalt splits into two components K₁ and K₂. The measurements given in Table I refer to the position of the K₁ component, which corresponds to the Fermi limit in the case of the metal and to the first available empty state in the compounds. It will be seen from Table I that the K absorption edge of cobalt is shifted in all the compounds towards the high energy side with respect to the discontinuity in the metal.

In column 5 of the table the values of the effective charges, calculated using Suchet's⁷ method,

TABLE I

Chemical shift of the K discontinuity of cobalt

Absorber	λ (X.U)	Energy ± 0.5 eV	ΔE (eV)	q (electrons atom)
Co metal	1604.70	7710.1		
CoAs	1603.75	7714.7	+ 4.6	+ 0.58
CoAs ₂	1604.20	7712.5	+ 2.4	+ 0.26
CoAsS	1603.29	7716.9	+ 6.8	+ 1.01
CoAs ₃	1604.03	7713.3	+ 3.2	+ 0.45
CoO	1602.80	7719.3	+ 9.2	+ 1.26
Co ₂ O ₃	1601.20	7727.0	+ 16.9	+ 1.80
CoCl ₂	1603.30	7717.3	+ 7.2	+ 1.10

are given. A plot of the chemical shifts *versus* the q values is shown in Fig. 1. The curve in the figure resembles the curves given by Sapre and Mande (1972, 1973) for the positive shifts and confirms that even in the case of the transition elements the chemical shift is governed by the effective charge on the absorbing ion. It is interesting to discuss here two special cases.

(i) Suchet's formula for the calculation of the effective charges is not directly applicable for ternary compounds. In the case of CoAsS we have assumed that the value of the charge on the cobalt ion in this compound is the average of the charges on the cobalt ions in CoAs₂ and CoS₂. The charge on the cobalt ion in CoAsS thus calculated comes out to be 1.01 electrons per atom. The corresponding point is seen to lie very well on the curve in Fig. 1.

(ii) According to Suchet the effective ionic charge is a result of two opposing causes: (a) the electronegativity difference between the constituent atoms which tends to bring them to complete ionic electronic configuration, and (b) the polarisation due to the interpenetration of the electronic clouds. The first effect renders the cobalt atom in the compound CoAs₃ in the Co⁺⁹ state in order to satisfy the valency 3 of the three arsenic atoms. Hence in this case the calculation of the effective charge on the cobalt ion requires datum on the ionic radius of Co⁺⁹ which is not available. We have estimated the effective charge on the cobalt ion in this compound from the curve in Fig. 1 and have obtained its value as 0.45 electrons per atom, which in turn gives the ionic radius of the Co⁺⁹ ion to be 0.5 Å. This value agrees very well with the value obtained by extrapolation of the curve 'ionic charge *versus* ionic radius' plotted with the available data.

Our results thus demonstrate the applicability of the chemical shifts in X-ray absorption spectra in the determination of the effective ionic charges and the ionic radii.

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POLY (BUTYL ACRYLATE-CO-METHYL METHACRYLATE) IN DILUTE SOLUTION

STUDIES on the solution properties of copolymers are not many in literature. Kotera *et al.*¹ have studied the solution properties of poly (methyl acrylate-co-methyl methacrylate). We report, here, the results of the investigations carried out on 1:1 poly(butyl acrylate-co-methyl methacrylate), PBMA, in methyl ethyl ketone and acetone.

From the reported² Q and e values the reactivity ratios r_1 and r_2 for butyl acrylate-methyl methacrylate copolymer were calculated. Bulk copolymerization of butyl acrylate and methyl methacrylate was carried out at 60° C in an atmosphere of nitrogen using α - α' azobisisobutyronitrile as initiator. Calculated amounts of the monomers were taken to get a copolymer of 1:1 composition and the conversion was restricted to ca 10%, so that the copolymer was homogeneous in composition. The polymer was purified and dried in vacuum at 55° C. It was fractionated into 10 fractions using methyl ethyl ketone, MEK, and methanol-water mixture as the solvent and precipitant respectively. Viscometry, osmometry and light-scattering experimental techniques and treatment of the data were the same as described earlier by Srinivasan and Santappa³.

RESULTS AND DISCUSSION

(i) The NMR spectrum of the copolymer in $CDCl_3$ at 56MC showed the ratio of the area of the O- CH_2 proton peak (at 4.76 τ) to that of the O- CH_3 proton peak (at 5.13 τ) to be unity, *i.e.*, the composition of the two monomers in the copolymer was 1:1. The (dn/dc) value was almost the same for all the samples (0.133 ± 0.004) in MEK indicating the narrow distribution of the constituents in the copolymer.

(ii) The polydispersity $(\bar{M}_w/\bar{M}_n) = 1.2$ was calculated from the ratio of the molecular weights obtained by light-scattering and osmometry and the heterogeneity factor $h = [(\bar{M}_w/\bar{M}_n) - 1]^{-1} = 5$ implied the narrow molecular weight distribution in the copolymer.

(iii) From the intercepts of the plots of η_{sp}/c vs c and $\ln \eta_{rel}/c$ vs c , $[\eta] = 222 - 442$ ml gm⁻¹ for PBMA/MEK system at 30° C and $[\eta] = 197 - 391$ ml gm⁻¹ for PBMA/Acetone system at 30° C for $\bar{M}_w = 0.9 - 3.0 \times 10^6$ were obtained. The Huggins constant k_1 ranged from 0.33 to

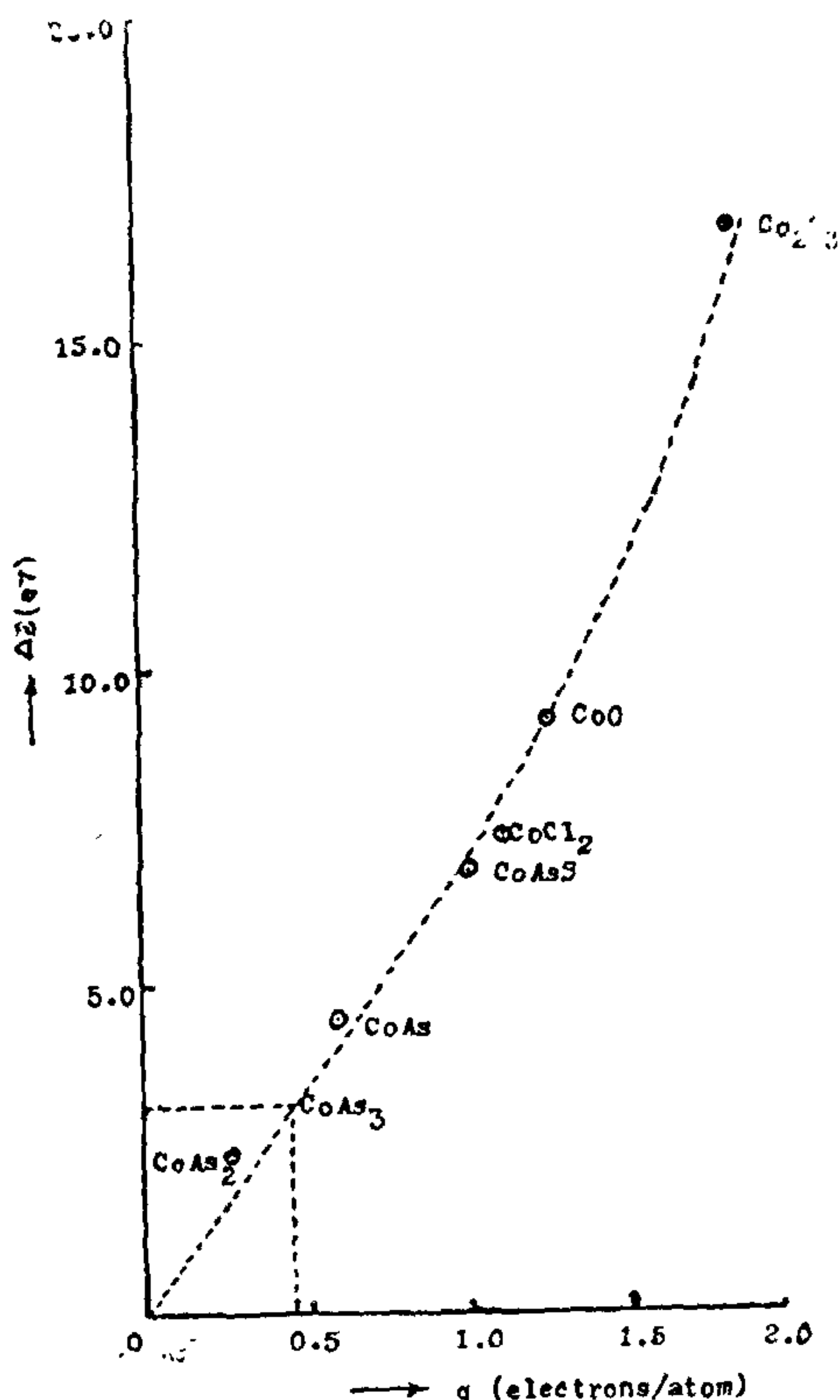


FIG. 1. Plot showing the dependence of the chemical shift ΔE , on the effective charge, q , for some cobalt compounds.

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