The Cathode-Ray Tube in X-Ray Spectroscopy and Quantitative Analysis

Under this title the Journal of the American Chemical Society has published a paper by us in the January number. A Coolidge tube was used, having a soldered aluminum window 6 mm in diameter and operated continuously at 0.2 m.a. and 85 kv D.C. Experiments were made with metal targets placed above the window and cooled with a jet of hydrogen. For the recording of the relative intensities of the $K\alpha$ doublet, primary attention was given to a method involving the application of an ionization chamber and an amplifying set. The latter made use of the new FP54 tube (Metcalf and Thompson, Phys. Rev. 36, 1489 (1930)). The smallest measurable grid current was 8.7 $(10)^{-16}$ amps. With a copper target and 0.4 mm slits, the peak of the $K\alpha$ doublet gave a net deflection of 90 cm with an accuracy of 0.5 cm on a scale 2.6 m distant, corresponding to an ionization current of 3 $(10)^{-13}$ amp.

The loss in electron velocity in passing through the window agreed with the Thomson formula. For molybdenum and iron the intensity was found to vary as the square of the difference between the electron velocity and the exciting voltage. This relationship held up to the maximum velocity employed, amounting to four-fold the exciting voltage for the case of molybdenum and eleven-fold for iron. Experiments as yet unreported are being made on titanium and calcium and the exponent has been found to be 1.3 for the voltage range extending from ten to sixteen-fold the exciting voltage. The exponent accordingly decreases less rapidly with increase in voltage than has been observed in similar experiments with x-ray tubes.

Curves showing the relation between chemical composition and the relative intensities of the unresolved $K\alpha$ doublets were obtained for copper-nickel and iron-nickel alloys—the latter representing the case in which the intensity of radiation from one constituent is increased as the result of excitation by the other.

Other experiments were carried out, using photographic recording by means of a Seemann spectrometer. For a molybdenum target, a 1° oscillation of the crystal and a slit width of 0.05 mm, a density of the $K\alpha_1$ line amounting to 0.4 was obtained by an exposure of sixteen minutes. Analyses by this method were made on silver-cadmium and tin-antimony alloys and the results were confirmed by chemical examination.

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The Hyperfine Structure of Ionized Lithium

The hyperfine structure of the low ${}^{3}P$ state of Li⁺ is of the same order of magnitude as the triplet separation itself. One might expect large deviations from the interval rule for hyperfine splitting, corresponding to large contributions of one triplet level to the perturbed eigenfunctions of another. Since the Li⁺ hyperfine structure has not yet been explained conclusively,¹ we have estimated the effect of these deviations on the calculated positions of the components. The resulting corrections are, however, small, and are not sufficient to give a better agreement than obtained by Güttinger.

Our method is simply to consider the transition between the extreme cases wherein the hyperfine splitting is either small or large com-

¹ H. Schüler, Zeits. f. Physik **66**, 431 (1930). P. Güttinger, Zeits. f. Physik **64**, 749 (1930). pared to the triplet separation. The coefficients of general equations for the levels were determined by use of the vector model in the extreme cases, and by using the usual identification of the lines for the isotope Li₆. The nucleus was considered as coupled only to the 1s electron in the ${}^{3}P$. About 6 percent was subtracted from the coupling constant as determined from the ${}^{3}S$, due to the interaction with the 2s electron there.² This correction alone has some effect on the results of Güttinger, as is indicated in the third column of the table.

In the case of $i=1\frac{1}{2}$, one of the coefficients of a cubic equation cannot be determined, and is represented by x in Table I. Its order of magnitude should be one-tenth cm⁻¹. Its evaluation would be intricate, but no value

² G. Breit and F. Doermann, Phys. Rev. **36**, 1732 (1930).

TABLE I.

				$i = 1\frac{1}{2}$				$i = \frac{1}{2}$	
Line ³	Schüler (exp.)		Güttinger		Extreme coupling	Intermed. coupling	Intermed. coupling		
1 2 3 4c 4b 4a 5b 5a 6c 6b 8c 8b 13b 13a 9 9	$\begin{array}{c} (0.5) 1 \\ (1) \\ (2) \\ (6) \\ (12) \\ (2) \\ (6) \\ (1.5) \\ (4) \\ (4) \end{array}$	8231.31 30.91 30.26 27.72 27.52 27.15 25.91 25.46 25.25	$(1) \\ (2) \\ (3) \\ (2) \\ (5.5) \\ (2) \\ (11) \\ (3) \\ (.5) \\ (2.5) \\ (2) \\ (2.5) \\ (.7) \\ (2) \\ (5.5) \\ (5.5) \\ (2) \\ (5.5) \\ (2) \\ (5.5) \\ (2) \\ (5.5) \\ (3) \\ (5.5) \\ (3) \\ (5) \\ ($	$\begin{array}{c} 31.31\\ 30.91\\ 30.25\\ 27.82\\ 27.74\\ 27.62\\ 27.56\\ 27.22\\ 27.22\\ 27.10\\ 25.96\\ 25.96\\ 25.56\\ 25.36\\ 25.23\\ \end{array}$	$\begin{array}{c} 31.31\\ 30.91\\ 30.26\\ 27.79\\ 27.88\\ 27.69\\ 27.58\\ 27.48\\ 27.29\\ 27.14\\ 26.03\\ 25.94\\ 25.63\\ 25.44\\ 25.29 \end{array}$	31.31 30.91 30.26 27.83 - x 27.97 - 3.1x 27.70 - x 27.58 - x 27.57 - 3.1x 27.30 - x 27.30 - x 27.18 - x 26.12 25.91 - x 25.72 25.44 - x 25.26 - x	(1) (2) (5) (9) (1) (1) (1) (2) (5)	30.91 30.26 27.56 27.39 26.91 25.80 25.51 25.15	

would bring much better agreement than was found in Güttinger's approximation. In the

⁸ The components 7, 11 and 14 are attributed to the Li⁶ isotope and have been omitted in this table. They are at 26.43, 24.33 and 29.48.

case $i=\frac{1}{2}$, our results give agreement just slightly worse than those quoted by Schüler.

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An Attempt to Detect Axiality of X-Ray Emission

J. Stark¹ has recently reported that fluorescent K-series x-rays are not emitted with equal intensity in all directions from certain crystals, and that these x-rays are at least partially plane-polarized. In the case of γ - γ dibromoanthracene, a monoclinic crystal of needle-like habit with the b-axis parallel to the length of the needle, he found about 20 percent more bromine K-radiation in directions 90° from the b-axis than in a direction 10° therefrom. The scattering of this radiation by aluminium indicated that it was polarized with the electric vector parallel to the b-axis. These effects are so important from the theoretical side that independent confirmation seemed desirable. This note reports an unsuccessful attempt to detect differences in the intensity of zinc K-radiation emitted in different crystallographic directions from a zinc crystal.

Zinc was chosen because the axial ratio for its hexagonal crystals, c/a = 1.86, is so much

¹ Stark, Ann. d. Physik [5] **6**, 637–662 (1930).

greater than that (1.63) to be expected in a close-packed arrangement of spheres that it is reasonable to suppose the atomic axes are not free to rotate about axes in the (001) plane. This is one of the criteria suggested by Stark for selecting materials likely to show the new effect. His objection to the use of metals, that the atoms therein are presumably free to rotate, does not therefore seem valid with respect to zinc.

The primary x-rays used were from a tungsten target tube operated at 55000 volts (peak) or from a molybdenum target tube operated at 44000 volts (peak). The zinc monocrystalline plate, 0.4 cm thick was rotated about its normal into various azimuths while its secondary radiation in a fixed direction 90° from the primary beam was measured by balancing its ionization with that of part of the primary beam. The absorption coefficient of the secondary radiation was found to be that of zinc K-radiation, indicating that the scattered radiation at 90° was negligible in comparison with the fluorescent. The normal to the plate was found by Laue and rotation