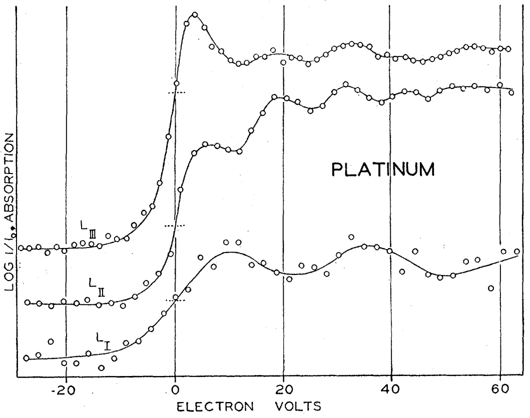

FIG. 10. L-absorption edges of platinum. Circles are experimental points. Positions of flex points are denoted by dashed lines. Edges are plotted to same energy scale and adjusted so that flex points coincide at point arbitrarily taken as the zero of the energy scale.

at the surface of the Fermi level. Because $6s$ electrons overlap more than do $5d$, one expects the $6s$ band to be broad, highly mixed, overlapping the $5d$. Due to the increase in nuclear charge in going from W to Pt, which contracts the electronic orbits, one expects all bands in Pt to be narrower and their states to show less mixing than in the corresponding bands of W. Again, the L absorption edges, shown in Fig. 10, are in agreement with the band picture. The L_{II} and L_{III} edges show a high initial absorption, while that of the L_I edge is small. There is much more structure corresponding to less mixing of states, due chiefly to the forbidding of $p \rightarrow p$ transitions in the L_{II} and L_{III} edges. It will be seen that although the positions of L_{II} and L_{III} structure features are in good agreement, their relative intensities are not. For example, the initial L_{III}-absorption peak is only a knee in the L_{II} edge. Differences in the L_{II} and L_{III} edges have also been recorded by other observers.[18] The L_{II} and L_{III} levels differ only in their j value. A large spin orbit coupling of the metallic valence electrons would suffice to account for these differences in a satisfactory manner.

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Fluorescent K X-Rays from Ions in Solution and from Gases

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The $K\alpha$ lines emitted by cobalt, nickel, copper and bromine contained in chemical compounds were compared with the lines emitted by these elements in pure form. Chemical combination was found to broaden the lines and increase their asymmetry. The magnitude of the effect was greatest for cobalt, progressively smaller for nickel and copper and completely unobservable in the case of bromine. The further effect on the $K\alpha_1$ lines of putting these compounds into water solution at various concentrations was studied. It was found that the lines were unchanged by solution regardless of the dilution. Finally, the $K\alpha$ doublets of liquid and gaseous bromine were studied and found to be identical, showing that the state of physical aggregation has no effect on the $K\alpha$ lines of this element.

INTRODUCTION

THE chemical state of an element is known to affect the shape, width, wave-length and relative intensity of its x-ray emission lines. Because the forces involved in chemical and physical binding are in no way greatly different, the physical state of an element is expected to affect its emission lines just as its chemical state does. However, as yet no dependence of the emission lines of a substance on its physical state has been found, although pronounced effects on the absorption spectra have been observed. Previous attempts to detect such an effect on the emission lines were of an indirect nature. They made use of the fact that the widths of the $K\alpha$ lines emitted by pure solid elements are smooth functions of the atomic number when it is sufficiently large. Because the widths of the $K\alpha$ lines from liquid gallium[1] and gaseous krypton[2] fell on these curves for solids, it was concluded that the widths were independent of the physical state. In the present work, a direct comparison is made between the x-ray lines emitted from different states of aggregation of the same substance. This provides a more delicate test for such effects. The $K\alpha$ doublet of gaseous bromine (Br_2) is compared with that of liquid bromine. The $K\alpha_1$ lines of crystalline compounds of the elements nickel, cobalt, copper and bromine are compared with the lines obtained from water solutions of these compounds. The lines emitted by solutions were studied over a wide range of concentrations.

EXPERIMENTAL

These studies were made possible by the improved intensity measuring technique of J. A. Bearden and C. H. Shaw,[3] which is especially useful for weak x-ray beams. This technique was applied in conjunction with a tube especially suitable for exciting high intensity secondary radiation. The tube was equipped with a gold-plated target cut at an angle of 45° to the axis of the tube. Primary radiation was taken off through a thin aluminum window. The secondary radiator, situated just outside of this window, was only $\frac{1}{4}''$ from the focal spot. Solid radiators were mounted on a metal support with a suitable adhesive. Gaseous and liquid radiators were contained in glass cells with very thin glass windows. These windows were made by heating the open end of a cell and pressing it while white hot into the side of a thin glass bubble. A single window of this type was used to pass both the exciting and the secondary radiation. The latter was taken off in a direction perpendicular to that of the incident primary beam and analyzed with a double crystal spectrometer which has been described elsewhere[4] as has the high voltage supply[5] for the tube. Intensities were measured with an argon-alcohol high pressure counter[6] in a multivibrator circuit[7] whose output fed through a scale-of-sixteen recorder[8] into a Cenco mechanical counter. Counting intervals were timed by a synchronous motor driven switch. With this apparatus, not only the fluorescent $K\alpha$ lines from bromine gas, but also those from nickel, present in water solution to only one part in 1250 by weight, were studied easily.

TABLE I. *Widths and indexes of asymmetry. In column 3* $K\alpha_1(1+1)$ *width is given in seconds except for the last two entries where the width is* $K\alpha_2(1+1)$*. In column 4 probable error (P.E.) is given in seconds. In column 5 the index of asymmetry, I, is listed.*

SUBSTANCE	STATE	WIDTH	P.E.	I	ΔW
(1)					
Cu	Metal	42.5	0.3	1.17	0.0
$CuSO_4$	Anhydrous powder	44.3	0.3	1.26	1.8
$CuSO_4 \cdot 5H_2O$	25% sol'n	45.3	0.3	1.22	2.8
$CuNo_3 \cdot 6H_2O$	Crystal	45.0	0.3	1.25	2.5
$CuNo_3 \cdot 6H_2O$	70% sol'n	45.0	0.3	1.24	2.5
(2)					
Cu	Metal	40.3	0.3	—	0.0
$CuSO_4 \cdot 5H_2O$	Crystal	43.0	0.3	1.21	2.7
(3)					
Cu	Metal	41.6	0.3	—	0.0
Ni	Metal	46.0	0.3	1.22	0.0
$NiSO_4 \cdot 7H_2O$	Crystal	56.3	0.3	1.89	10.3
$NiSO_4 \cdot 7H_2O$	16% sol'n	56.0	0.3	1.81	10.0
$NiSO_4 \cdot 7H_2O$	4% sol'n	56.3	0.5	1.7	10.3
$NiSO_4 \cdot 7H_2O$	0.4% sol'n	56	1.0	1.7	10
Co	Metal	57.4	0.5	1.4	0.0
$CoCl_3 \cdot 6H_2O$	Crystal	84.3	0.5	1.65	26.9
$CoCl_3 \cdot 6H_2O$	10% sol'n	84.3	0.9	1.67	26.9
$CoCl_3 \cdot 6H_2O$	4% sol'n	84	1.4	1.7	26.6
Br_2	Liquid	29.5	0.5	1.0	0.0
Br_2	Gas	29.5	0.5	1.0	0.0
KBr	Crystal	30	1.6	1.0	0.5
KBr	1% sol'n	29.6	2.0	1.0	0.1
$CuBr_2$	Crystal	29.9	0.5	1.0	0.4
Br_2	Liquid	30.5	0.5	1.0	0.0
Br_2	Gas	31	1.0	1.0	0.5

DISCUSSION OF RESULTS

In Table I are given the widths and indexes of asymmetry of the lines studied. The increase in

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width, ΔW, over that obtained for a pure element in its normal state, is also listed. These measurements were made in three groups. Between groups, because the spectrometer crystals were removed and replaced, the line widths obtained were altered. In a single group of measurements the crystal characteristics remained fixed. To compare results in different groups the $(1+1)$ widths of Cu $K\alpha_1$ are given for reference at the beginning of each group.

A comparison of the lines emitted from these elements in compounds with those emitted by the same elements in pure form shows that the effect of chemical combination is to broaden the lines and increase their asymmetry. The magnitude of the effect is seen to vary from element to element. In the case of bromine the lines of Br_2, KBr and $CuBr_2$ were found to be identical within the experimental error. In the case of copper, the lines of both the nitrate and the sulphate were several seconds broader and somewhat less symmetrical than that of the metal. The nickel sulphate line was $10''$ wider and very much more asymmetrical than that of pure nickel, and the $CoCl_3 \cdot 6H_2O$ line was $27''$ wider than that of cobalt although the change in asymmetry was not as marked as in the case of the nickel salt.

It is expected that those features of x-ray emission lines that are sensitive to chemical combination should also be sensitive to changes in physical state. A comparison of widths and asymmetries of lines emitted from different physical states of a substance should reveal the effect of such a change. It will be seen that the $K\alpha_{1,2}$ doublets of gaseous and liquid bromine are the same and furthermore that the $K\alpha_1$ line of KBr is the same whether the substance is in crystalline form or in rather dilute aqueous solution. From the fact that the $K\alpha$ lines of bromine showed no dependence on its chemical state, no dependence of these lines on the physical state is to be expected, due to the similar nature of the two effects.

In the cases of copper, nickel and cobalt where there is a very marked chemical effect, however, no dependence on the physical state is observed either. The lines from crystalline solids and their solutions are the same. However, there is a difference between the lines from the anhydrous and hydrated salt in the case of $CuSO_4$. These facts may be understood when one considers that in order to eliminate chemical changes on putting the compounds into solution only those compounds were used in which the metallic ions were already surrounded by the appropriate number of coordinated water molecules which they would otherwise acquire on solvation. Each ion in the hydrated crystals used, then, is protected from the action of external forces by a layer of surrounding water molecules which one may conveniently consider as an equivalent layer of dielectric constant 81. This layer is introduced into the crystal on transforming the anhydrous to the hydrated form. It reduces the Coulomb forces between ions by a factor greater than 81. The effect of thickening this layer of water, which is effectively what happens on putting the salt into solution, is to reduce this already small force to zero. The main effect occurs then, on introducing the first layer of water molecules; the effect in the case of $CuSO_4$ is seen to be comparable to that of chemical combination. The effect of putting such a hydrated salt into solution should be expected even in the case of cobalt to produce a change in line width of less than $0.25''$. As this quantity is considerably smaller than the experimental error, it is understood why no effect on the $K\alpha_1$ line width of these compounds due to putting them into solution was found.

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