$$F_1(M) = \sum_{k=0}^{n} \frac{k!(-1)^k}{b^{k+1}} \frac{(M-k-2)!}{(a+b)^{M-k-1}} + R_n, \quad \text{where } |R_n| < \frac{(n+1)!}{b^{n+2}} \frac{(M-n-3)!}{(a+b)^{M-n-2}}$$

was used for a fairly high value of M, together with a backwards recursion formula. The scheme can be checked by noticing that $F_1(1) = (1/a)\ln[(b+a)/b]$. Once $F_N(M)$ has been found for $N=1$, it is a simple matter to calculate the integrals for $N=2, 3$ and 4 by partial integration.

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Experimental Evidence for the Parratt X-Ray Excitation Theory*

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The intensity distribution of the Cr $K\alpha_1$ line in Cr metal and some of its (II) and (III) valence halides has been studied by means of a high-resolution x-ray spectrometer. It is found that while the $K\alpha_1$ line appears continuous in the metal, it splits up in the (II) and (III) valence compounds, the magnitude of splitting being 0.21 ± 0.03 eV and 0.29 ± 0.03 eV, respectively. The results obtained are interpreted by considering a new aspect about the formation of the energy levels. These levels could be taken as made up of ionization states split into sublevels owing to the exchange interaction between $2p$, $3d$ electrons and the excitation states. This provides evidence for the excitation states in solids as proposed by Parratt in his modified x-ray energy-level diagram.

INTRODUCTION

A new approach to the investigation of the x-ray excitation states in solids is presented. The fundamental excitation-level[1] aspects first used by Landshoff[2] and later by Cauchois and Mott[3] to explain the absorption edge structure have been incorporated into a more general theory by Parratt.[4] In his modified x-ray energy-level diagram Parratt proposes two types of excitation states. One type, the bound-ejected-electron excitation state (BEE), is characterized by the assumption that the ejected electron resides in one of the bound orbitals. The other type, the valence-electron-configuration excitation states (VEC), are those produced due to regrouping of valence electrons as a consequence of a change of wave functions of the electrons in the atom when an inner vacancy is created. In addition there are also present the states called ionization or unexcited states which refer to the limiting case when the ejected electron approaches infinity with zero kinetic energy.

In Fig. 1 we show a qualitative energy-level diagram according to Parratt. It is shown that each single energy level in a conventional diagram is split up into a continuum and a set of discrete excitation states represented by the symbols ν, σ, and ρ. However, the excitation states of BEE type are believed to be rarely produced by bombardment of electrons on the anode. Further, an x-ray energy level is also expected to become split as a result of exchange interaction between the electrons of the $2p$ and the incomplete $3d$ subshell. Meisel and Nefedow[5] have explained the observed multiplet structure of the Cr $K\alpha_1$ line in Cr_2O_3 by considering such interactions. However, it is stated that this type of splitting should be very small in magnitude and should rather affect the width and asymmetry of the emission line.

The first experimental investigation of the Parratt theory was made by Johansson,[6] who tried to determine the position of the Cr $K\alpha_1$ line at the threshold voltage and at 3 kV above it, i.e., by changing the energy states involved in the $K\alpha_1$ line emission. Johansson did find a shift of the order of 0.1 eV, but unfortunately the experimental error was also of the same magnitude. We have therefore attempted an alternative method by studying the effect of the change in valence electron configuration on the $K\alpha_1$ line when going from metallic Cr to Cr (II) and Cr (III) halides. Since this splitting was first found in Cr (III) oxide in emission,[5,7] we have included this compound for comparison.

RESULTS AND DISCUSSION

The experiment has been performed using a high-resolution x-ray spectrometer of Johann type, described in the earlier publication,[8] with a dispersion of 0.298 mm/eV. The compounds were either pressed on the meshed anode or evaporated onto a clean anode surface. The working pressure in the x-ray tube was always in the μTorr range, and the tube was operated at 7 kV and 5 mA. The intensity distribution of the $K\alpha$ lines was recorded by moving the slit along the tangent of the Rowland circle.

The $K\alpha_1$ line was found to be split in both Cr (II) and Cr (III) valence compound, but such a splitting was not observed in case of Cr metal. As can be seen in Table I, the order of the splitting amounts to about 0.21 and 0.29 eV, respectively. The splitting could be seen in the curves shown in Fig. 2 for Cr_2O_3 and CrF_3. In the case of the metal, although VEC excitation states may be present, the energy difference between these states and ionization states is so small that the $K\alpha_1$ line does not

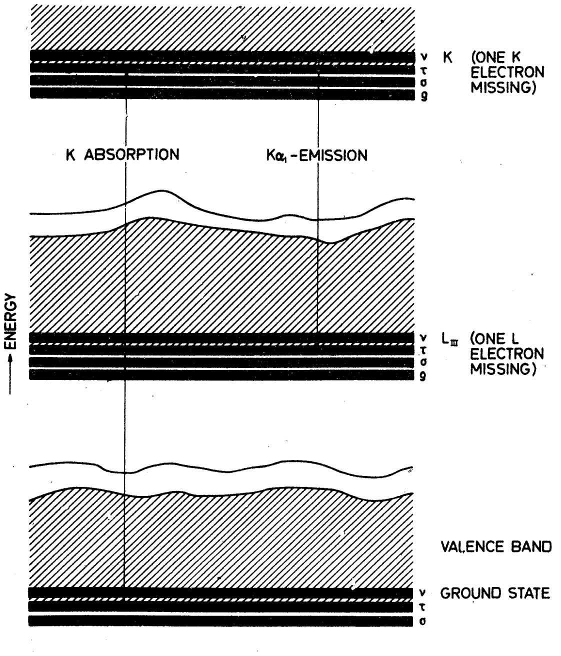

FIG. 1. Energy-level diagram for a metal as proposed by Parratt (Ref. 4).

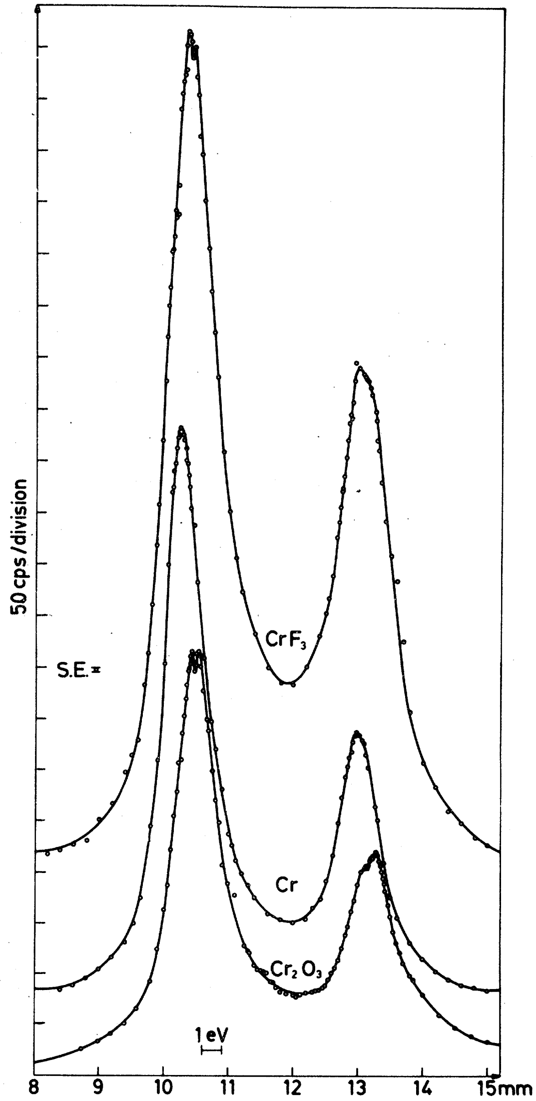

FIG. 2. Intensity distribution of the $K\alpha$ emission lines for Cr, Cr_2O_3, and CrF_3.

TABLE I. Experimental line shifts and multiplet splittings in eV.

Compound	Valency of Cr atom	Shift of total $K\alpha_1$ line with respect to Cr metal	Energy separation of multiplets
$CrCl_2$	II	0.03	0.21 ± 0.03
CrF_2	II	0.00	0.20 ± 0.03
			Mean = 0.21 ± 0.03
$CrCl_3$	III	0.44	0.27 ± 0.03
CrF_3	III	0.47	0.31 ± 0.03
Cr_2O_3	III	0.57	0.28 ± 0.03
			Mean = 0.29 ± 0.03

show any structure. As stated above the question of BEE excitation states does not arise, and neither is the *j-j* coupling expected to play any prominent role. But as one goes to (II) valence compounds, thereby initiating a change in the valence electron configuration, the energy separation between the excitation and ionization states becomes more pronounced. It is rather difficult at this stage to estimate the role played by *j-j* coupling even though, according to Nefedov,[9] it is solely the interaction of the $2p$ and $3d$ electrons that gives rise to the multiplet structure. However, it seems reasonable to expect that such interaction, which is no doubt present, should cause an increase in the energy separation between the ionization and the excitation state, which in turn gives the observed splitting. Further support of this is found in the observed increased magnitude of the splitting for the (III) valence halides. Here an additional decrease in the number of valence electrons occurs which changes the strength of the *j-j* coupling. The increase in the energy separation between the different states may be attributed to this change. From the above discussion, the inclusion of the excitation states in the x-ray energy level seems to be unavoidable.

It must, however, be remarked that recently it has been shown by means of electron bombardment and K capture experiments[10,11] that the relaxation time of the system τ_h is much less than the K-state lifetime. Hence it appears that as a result of the K ionization, multiple ionization or excitation states are possible, but less probable. Moreover, Tsutsumi[12] has reconsidered the exchange interaction between the electrons of the incomplete $3d$ subshell and those of the $2p$ subshell after the creation of a vacancy. It is the intention of the authors to consider these various aspects in detail in their forthcoming paper.[13]

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[1] The term excitation and exciton level are used in the conventional way; i. e., "exciton" is commonly used in reference to one type of excitation state produced due to coupling of electrons and positive holes in absorption spectra, especially in the ultraviolet region. The analogous term for the x-ray spectra is "excitation state."

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