## Comments

*Comments are short papers which comment on papers of other authors previously published in the* **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

# Electron-electron interaction in transition-metal x-ray emission spectra

K. S. Srivastava, Shiv Singh,* A. K. Srivastava, R. S. Nayal, Amita Chaubey, and Pratibha Gupta

*Theoretical Physics Division, Physics Department, Lucknow University, Lucknow 226007 (U.P.), India*

(Received 23 December 1980)

An alternative explanation for the origin of the $K\beta'$ satellite of the $K\beta_{1,3}$ x-ray emission line of the first transition elements ($21 \leq Z \leq 29$) has been given using the Bohm and Pines theory of plasma oscillations in solids. The present calculated values for the energy separation ($\Delta E$), and the relative intensity of the $K\beta'$ satellite with respect to the $K\beta_{1,3}$ x-ray emission line, agree better with the experimentally observed values than the values calculated by the exchange-interaction theory of Tsutsumi *et al.*, Salem *et al.*, and Ekstig *et al.*

## I. INTRODUCTION

X-ray satellites are relatively weak lines often observed close to the main x-ray diagram lines. The energy of these lines cannot be expressed as the difference of two levels in the conventional energy-level diagram. For this reason these satellite lines are often called nondiagram lines. There exist a number of theories[1-3] which can satisfactorily explain the origin of those x-ray satellites which are found on the high-energy side of the x-ray diagram lines, often abbreviated as high-energy satellites (HES). However, there is no theory which can account for the existence of the low-energy satellites (LES) which are found on the low-energy side of the parent diagram line. In particular, the origin of the $K\beta'$ satellite of the $K\beta_{1,3}$ emission line, which have been observed by several workers[4-17] in the elements ($21 \leq Z \leq 29$) of the first transition series, lack proper explanation.

Several researchers[4-17] have proposed from time to time explanations for the origin of the $K\beta'$ satellite. Tsutsumi,[9] Parratt,[10] and Ekstig *et al.*[13] have reviewed the various theories for the $K\beta'$ satellite; however, none of these theories can account satisfactorily for either the energy separation or the relative intensity. In this paper, we propose a theory based on plasmon oscillations in solids and compare our results with earlier theoretical and experimental findings.

## II. PREVIOUS THEORIES

Deodhar's theory based on double ionization[6] and Sawada's theory invoking two-electron transitions[7] were both rejected by Tsutsumi[9] since the observed excitation voltage for the $K\beta'$ satellite is lower than what is predicted by both these theories. Parratt[10] proposed that the $K\beta'$ satellite originated from $1s$ hole states with excited valence electron configuration (VEC) states but his hypothesis was disapproved by Schnopper,[18] who studied the $K\beta'$ satellite of $1s$ hole states of Mn originating from $K$ capture of $^{55}$Fe and found no difference to the emission from states produced with electron excitation. In the former case there would be little change in the effective potential experienced by the valence electrons and thus low probability for the production of VEC states compared with the electron excitation method. Coster and Druyvesteyn[5] had proposed that the $K\beta'$ structure originates from the interaction between a hole and the incomplete $3d$ shell. This hypothesis was extended by Tsutsumi[9] and Tsutsumi *et al.*[11,12] According to them the origin of the $K\beta'$ line is derived from the exchange interaction between the electrons in the incomplete $3d$ shell of elements in the first transition series and the hole in the incomplete $3p$ shell, owing to the emission of the $K\beta_{1,3}$ line. Thus, the $K\beta_{1,3}$ and $K\beta'$ lines are emitted by transition to the states having the total spins equal

 

to $S+\frac{1}{2}$ and $S-\frac{1}{2}$, respectively, where $S$ is the total spin of the incomplete $3d$ shell and $\frac{1}{2}$ is that of the incomplete $3p$ shell in the final state having one vacancy in the $3p$ shell, owing to the transition of an electron from the complete $3p$ shell to the $1s$ shell by the emission of the $K\beta_{1,3}$ line. A similar theory has also been proposed by Salem *et al.*[17] according to which the exchange interaction between the $3d$ and $3p$ electrons splits both levels, causing some of the electrons in the $3p$ state to move to lower energy levels; transition from these levels appear as the $K\beta'$ emission satellite on the low-energy side of the $K\beta_{1,3}$ line. The energy difference between $K\beta_{1,3}$ and $K\beta'$ lines would then correspond to the difference between the exchange energies of $S+\frac{1}{2}$ and $S-\frac{1}{2}$ states. The exchange interaction of the state having a total spin $(S+s)$ is given by[19,20]

$$-\tfrac{1}{2}J(1+4S\cdot s)\ ,$$

where $J$ is the exchange integral,[21] $S$ is the total spin vector of the incomplete $3d$ shell, and $s$ is that of the $3p$ shell. For the transition metals, $J$ can be expressed in terms of Hartree-Fock-Slater integrals[21] $G^1$ and $G^3$ as

$$J=[\tfrac{2}{15}G^1(3p,3d)+\tfrac{3}{35}G^3(3p,3d)]\ . \qquad (1)$$

[There is a printing error in the paper of Salem *et al.*[17] in the numerical coefficient of $G^3$ in Eq. (1). The correct numerical coefficient of $G^3$ should be $\frac{3}{35}$ rather than $\frac{3}{15}$ as mentioned in Ref. 17.] The values of $G^1$ and $G^3$ have been computed by Mann.[22] The magnitude of the energy difference $\Delta E$ between the exchange interaction for $S+\frac{1}{2}$ and for $S-\frac{1}{2}$ states is given by

$$\Delta E=J[(S+\tfrac{1}{2})(S+\tfrac{1}{2}+1) -(S-\tfrac{1}{2})(S-\tfrac{1}{2}+1)]=J(2S+1)\ . \qquad (2)$$

From Eqs. (1) and (2) we can also have

$$\Delta E=[\tfrac{2}{15}G^1(3p,3d)+\tfrac{3}{35}G^3(3p,3d)](2S+1)\ . \qquad (3)$$

The relative intensity $I'/I$ of the $K\beta'$ to $K\beta_{1,3}$ lines is estimated from the ratio of the multiplicity of each state, that is,

$$i=I'/I=\frac{2(S-\frac{1}{2})+1}{2(S+\frac{1}{2})+1}=\frac{S}{(S+1)}\ . \qquad (4)$$

Using Eqs. (3) and (4), Tsutsumi *et al.*[9,11,12] have calculated the values of $\Delta E$ and $i$ for some transition elements. However, their results give only an order of magnitude agreement (see Tables II and III). Ekstig *et al.*[13] have also tried to explain the origin of the $K\beta'$ satellite by considering the initial state of the emission process as consisting of the $1s$ hole coupled to the ground term of the corresponding $3d^n$ configuration. Assuming that this $d^n$ term has the orbital angular momentum $L_0$ and the spin $S_0$, the two new $1s\,3d^n$ terms can be described by the quantum numbers $(L_0, S_0+\frac{1}{2})$ and $(L_0, S_0-\frac{1}{2})$. The energy splitting between these two terms estimated from Clementi's[23] wave functions is of the order of 0.04 eV. It is obvious that this splitting is too small to be observable.

The final state of the $K\beta_{1,3}$ emission has the configuration $(3p^5 3d^n)$, that is, the original $1s$ hole has been filled by a $3p$ electron. In general, six terms arise with quantum numbers $L=L_0-1$, $L_0$, or $L_0+1$ and $S=S-\frac{1}{2}$ or $S+\frac{1}{2}$. Here all hole states are described in the frozen electron approximation, that is, with the same orbital wave function as the neutral ground state. Under these circumstances, and neglecting the energy dependent factor, Ekstig *et al.*[13] have shown that the relative transition probabilities are proportional to $(2S+1)(2L+1)$, the same result as that obtained by Tsutsumi *et al.*[9,11,12] and Nefedov.[14]

Recently, Salem *et al.*[17] have studied the low-energy $K\beta'$ satellite in the $K\beta_{1,3}$ x-ray emission spectra of transition elements Sc, Ti, V, Cr, Fe, Co, Ni, and Cu, both in the metallic state, as well as in the following oxidized states: CuO, NiO, $Co_3O_4$, $Fe_2O_3$, $MnO_2$, $Cr_2O_3$, VO, and $TiO_2$. They have compared their observed values with the calculated values obtained from formulas (3) and (4) of Tsutsumi *et al.*[9,11,12] for the energy separation and relative intensity, respectively. They have also stated that the exchange interaction between the $3d$ electrons and the $3p$ hole in these metals causes some of the $3p$ electrons to move to lower energy levels. Transitions from these levels appear as the satellite $K\beta'$ on the low-energy side of the diagram line $K\beta_{1,3}$. However, as shown in Table III and Fig. 2, there is considerable disagreement between the observed and the calculated values of the relative intensities of the $K\beta'$ satellites. Furthermore, Salem *et al.*[17] have not given any calculated numerical value for the energy separation and relative intensity of the $K\beta'$ satellite of the following oxidized states: $TiO_2$, VO, $Cr_2O_3$, $MnO_2$, $Fe_2O_3$, $Co_3O_4$, NiO, and CuO.

It was therefore thought of interest to attempt to explain the origin of the $K\beta'$ satellite by an alternative theory. We present in this paper a theory based on plasmon oscillations. Though the

exchange-interaction theories of Salem *et al.*[17] and Tsutsumi *et al.*[9,11,12] may also be valid, it will be seen that our calculated values for relative intensity and energy separation are in better agreement with the experimental values than are the values calculated on the basis of exchange-interaction theories.[9,11,12,17]

## III. PLASMON THEORY

The theory of plasmon oscillation in solids is fairly close to the suggestion of Blochin[8] in that part of the energy quantum of the $K\beta_{1,3}$ line may be absorbed by $3d$ electrons giving rise to the low-energy $K\beta'$ satellite. This approach was quite appropriate but Blochin could not explain how much energy will be shared by the $3d$ electron and what might be its final state. Tsutsumi[9] rejected the above approach without assigning any reason.

According to the plasmon oscillation theory, during the x-ray emission process, the transiting valence electron excites a plasmon in the valence band. The transition energy of the $K\beta_{1,3}$ line will thus be shared between the plasmon and the emitted photon which will thus be deprived of an energy equal to the plasmon energy ($\hbar\omega_p$) used up in exciting the plasmon. Thus, this process will give rise to the emission of a low-energy x-ray plasmon satellite $K\beta'$. Such low-energy satellites have been observed by several workers[24–32] in several metals and their compounds, and a few of them have been explained by the theory of plasmon oscillation merely on the basis of their energy separation from the parent emission line. In the present paper, we use the plasmon oscillation theory to calculate not only the energy separation but also the intensity of the low-energy satellite $K\beta'$ relative to the parent diagram line $K\beta_{1,3}$. It is seen that there is fairly good agreement between our calculated values and the observed values of Salem *et al.*[15–17] and Tsutsumi *et al.*[9,11,12] for both the energy separation as well as the relative intensity except in Sc, where the $d$ level has just one electron, and in Cu, where the $d$ shell is almost completely filled.

## IV. ENERGY SEPARATION ($\Delta E$) OF THE $K\beta'$ SATELLITES

According to what has been said above, the energy separation ($\Delta E$) of the low energy $K\beta'$ satellite from the $K\beta_{1,3}$ ($KM_{2,3}$) emission line should equal the quantum of plasmon energy $\hbar\omega_p$ which can be calculated by the formula given by Marton *et al.*[33] as

$$\hbar\omega_p = 28.8\left[\frac{Z\sigma}{W}\right]^{1/2}\text{eV}, \tag{5}$$

where $Z$ is the effective number of electrons taking part in plasmon oscillations, $\sigma$ is the specific gravity, and $W$ is the molecular weight.

Equation (5) is valid for the free electron model, but to a fairly good approximation it can also be used for semiconductors and insulators. According to Kittel,[34] plasma oscillations in dielectrics are physically the same as in metals. This fact can be substantiated by the work of Raether,[35] and Philipp and Ehrenreich[36] who have shown, after taking into account the band sctructure of solids, that the plasma frequency for dielectrics is

$$\omega_{pd}^2 = \frac{\omega_p^2}{(1-\delta\epsilon_0)}, \tag{6}$$

where $\delta\epsilon_0$ is a very small quantity, and can be neglected in a first approximation. Philipp and Ehrenreich[36] have shown that the calculated values of $\hbar\omega_p$ and $\hbar\omega_{pd}$ are in fair agreement with their observed values of plasmon energy for dielectrics.

The recent data[37–40] on the plasma loss values in transition elements show that the effective number of electrons taking part in plasma oscillations is one, because from Sc to Cu ($3d^n4s^1$), the $d$ electrons are highly localized, and so only the $4s^1$ electron can take part in plasmon oscillations. Thus, the value of $Z$ is one for all transition elements in Eq (5). This fact has also been shown recently.[40] Glasstone[41] has shown that in the case of oxygen the number of unpaired electrons is two. Hence, $Z=2$ for oxygen. Taking the values of $Z$, $\sigma$, and $W$ from Table I and using Eq. (5), the values of plasmon energy ($\hbar\omega_p$) have been calculated (see Table I). They are found to be fairly close to the experimentally observed[17] values of the energy separation ($\Delta E$) of the $K\beta'$ satellite from $K\beta_{1,3}$ emission line (see Table II and Fig. 1). In the case of metals, volume plasmons are excited (see Tables I and II), while in case of oxides, only surface plasmons are excited. Thus, the $K\beta'$ satellite in transition metals is due to the excitation of volume plasmon, while in case of compounds it is due to surface plasmon excitation. Hence, from energy considerations alone, the $K\beta'$ satellite in transition elements and their compounds can be regarded as being due to the excitation of volume and surface plasmons, respectively.

## V. RELATIVE INTENSITY OF THE $K\beta'$ SATELLITE

Further confirmation of the origin of the $K\beta'$ satellite can be made by calculating intensity rela-

TABLE I. Plasmon energy of transition elements.

| Serial No. | Element/ compound | $Z$ | $\sigma$ | $W$ | $\hbar\omega_p = 28.8\sqrt{Z\sigma/W}$ (eV) | $\hbar\omega_s = \frac{\hbar\omega_p}{\sqrt{2}}$ Surface plasmon loss (eV) | $r_s = \left[\frac{47.11}{\hbar\omega_p}\right]^{2/3}$ |
|---|---|---|---|---|---|---|---|
| 1 | Sc | 1 | 2.5 | 44.96 | 6.79 | | 3.6377 |
| 2 | Ti | 1 | 4.5 | 47.90 | 8.83 | | 3.0533 |
| 3 | $TiO_2$ | 5 | 3.84 | 79.90 | 14.12 | 9.98 | 2.8140 |
| 4 | V | 1 | 5.96 | 50.95 | 9.85 | | 2.8387 |
| 5 | VO | 3 | 5.758 | 66.95 | 14.63 | 10.34 | 2.7483 |
| 6 | Cr | 1 | 7.20 | 52.01 | 10.72 | | 2.6830 |
| 7 | $Cr_2O_3$ | 8 | 5.21 | 152.02 | 15.08 | 10.66 | 2.6930 |
| 8 | Mn | 1 | 7.20 | 54.94 | 10.43 | | 2.7325 |
| 9 | $MnO_2$ | 5 | 5.026 | 86.93 | 15.48 | 10.95 | 2.6452 |
| 10 | Fe | 1 | 7.86 | 55.85 | 10.80 | | 2.6697 |
| 11 | $Fe_2O_3$ | 8 | 5.24 | 159.70 | 14.76 | 10.43 | 2.7325 |
| 12 | Co | 1 | 8.90 | 58.94 | 11.19 | | 2.6073 |
| 13 | $Co_3O_4$ | 11 | 6.07 | 240.82 | 15.16 | 10.72 | 2.6830 |
| 14 | Ni | 1 | 8.90 | 58.71 | 11.21 | | 2.6042 |
| 15 | NiO | 3 | 7.45 | 74.69 | 15.75 | 11.14 | 2.6151 |
| 16 | Cu | 1 | 8.92 | 63.54 | 10.79 | | 2.6713 |
| 17 | CuO | 3 | 6.40 | 79.54 | 14.15 | 10.01 | 2.8084 |

TABLE II. Energy separation ($\Delta E$) of the $K\beta'$ satellite lines.

| | | Tsutsumi *et al.* (Refs. 9, 11, 12) $\Delta E$ | | Salem *et al.* (Ref. 17) $\Delta E$ | | Authors $\Delta E$ |
|---|---|---|---|---|---|---|
| Serial No. | Element/ compound | Calc. (eV) | Obs. (eV) | Calc. (eV) | Obs. (eV) | plasmon loss (eV) |
| 1 | Sc | | | 3.71 | 5.73±0.86 | 6.79 |
| 2 | Ti | | | 6.22 | 7.08±0.71 | 8.83 |
| 3 | $TiO_2$ | | | | 5.08±0.70 | 9.98 |
| 4 | V | | | 9.07 | 10.24±1.09 | 9.85 |
| 5 | VO | | | | 9.51±1.0 | 10.34 |
| 6 | Cr | 1.77 | 8.3 | 13.35 | 11.04±1.11 | 10.72 |
| 7 | $Cr_2O_3$ | 5.88 | 12.8 | | 10.62±1.1 | 10.66 |
| 8 | Mn | 3.55 | 9.02 | 15.65 | 12.28±1.2 | 10.43 |
| 9 | $MnO_2$ | 7.36 | 14.72 | | 12.87±1.3 | 10.95 |
| 10 | Fe | | | 13.84 | 11.71±1.2 | 10.80 |
| 11 | $Fe_2O_3$ | 9.72 | 14.19 | | 13.36±1.3 | 10.43 |
| 12 | Co | | | 11.69 | 11.54±1.1 | 11.19 |
| 13 | $Co_3O_4$ | | | | 12.19±1.2 | 10.72 |
| 14 | Ni | | | 9.22 | 12.98±1.9 | 11.21 |
| 15 | NiO | | | | 11.29±1.7 | 11.14 |
| 16 | Cu | | | 0.00 | 12.34±2.4 | 10.79 |
| 17 | CuO | | | | 12.81±2.5 | 10.01 |

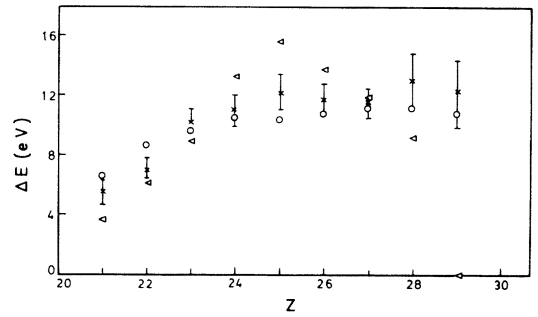


FIG. 1. Comparison of our results for the energy separation of the $K\beta'$ satellite with respect to the $K\beta_{1,3}$ x-ray emission line in transition elements with the results of Salem *et al.*[○ authors; ×, Salem *et al.* (obs.); Δ Salem *et al.* (calc.)].

tive to the $K\beta_{1,3}$ line. Langreth[42–44] and Chang and Langreth[45] have developed a general theory to explain the presence or absence of plasmon satellites in soft x-ray spectroscopy (SXS), x-ray photoelectron spectroscopy (XPS), soft x-ray appearance potential spectroscopy (SXAPS), etc., experiments, and differentiated between extrinsic and intrinsic coupling processes. An extrinsic effect is generally associated with an energy-loss process, while an intrinsic effect is important for plasmon satellites. They have further classified the intrinsic effect into two types of processes: (1) those in which the number of slow electrons is not conserved, e.g., in SXAPS and XPS, etc., experiments and in which case plasmon satellites will be strong if the coupling constant is sufficiently large; and (2) those in which the number of slow electrons is conserved, e.g., in SXS experiments and in this case plasmon satellites will be weak even though the coupling constant itself, may be large.

Following Langreth[43] the transition probability $P(\omega)$ per unit time per unit energy range at energy $\hbar\omega$ for the emission of a plasmon satellite is given by

$$P(\omega)=|f|^2\sum_n e^{-\alpha}\frac{\alpha^n}{n!}\delta(\omega-\epsilon_h-\alpha\omega_p+n\omega_p)\ , \quad (7)$$

where $\alpha$, the coupling parameter,[42–45] is given by

$$\alpha=\frac{e^2q_{\max}}{\pi\hbar\omega_p}\simeq 0.12r_s\ , \quad (8)$$

$f$ is the matrix element for the process, $q_{\max}$ is the plasmon cutoff wave vector, and $r_s$ is a dimensionless parameter[46] given by

$$r_s=\left[\frac{47.11}{\hbar\omega_p}\right]^{2/3}. \quad (9)$$

The weight factor $e^{-\alpha}\alpha^n/n!$ in Eq. (7) represents[42] the strength of the $n$th satellite ($n=0$ represents the main peak). Thus, the relative intensity of the first plasmon peak to the main peak in fluorescent excitation is given by

$$i=\frac{I_1}{I_0}=\alpha=0.12r_s\ . \quad (10)$$

The coupling parameter $\alpha$ can further be modified[45] by taking into account the effect of "slow-fast" interference terms which produce the cancellation when a "slow" charge is conserved. The effect[42–45] of the interference term is to modify $\alpha$ to a new coupling parameter:

$$\alpha'=\alpha-\left[\frac{e^2}{\hbar v}\right]F\ , \quad (11)$$

where $F$ is a slowly varying function of velocity and has a value very nearly equal to unity. The value of $(e^2/\hbar v)$ has been calculated[42–45] to be of the order of 0.1 for incident energies of the order of keV, so that $\alpha'$ is given by

$$\alpha'=\alpha-\frac{e^2}{\hbar v}=0.12r_s-0.1\ . \quad (12)$$

Thus, using Eqs. (9)–(12) we have the relative intensity of the $K\beta'$ satellites as

$$i=\frac{I_1}{I_0}=\alpha'=0.12r_s-0.1\ . \quad (13)$$

The calculated values of $i$ for transition metals and their oxides are given in Table III, in which the results have also been compared with those of oth-

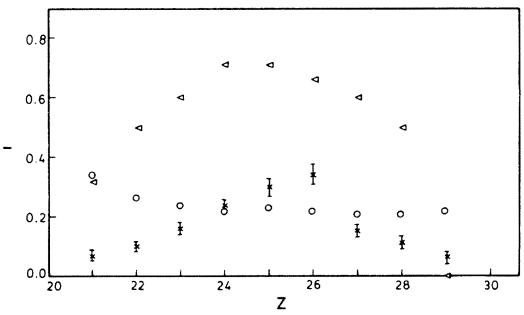


FIG. 2. Comparison of our results for the relative intensity of the $K\beta'$ satellite with respect to the $K\beta_{1,3}$ x-ray emission line in transition elements with the results of Salem *et al.* The symbols in the figures stand for the following: ○, authors; ×, Salem *et al.* observed; △, Salem *et al.* calculated.

TABLE III. Relative intensity $i$ of the $K\beta'$ satellite lines.

| Serial No. | Elements/ compound | Tsutsumi *et al.* (Refs. 9, 11, 12) Calc. | Tsutsumi *et al.* (Refs. 9, 11, 12) Obs. | Salem *et al.* (Ref. 17) Calc. | Salem *et al.* (Ref. 17) Obs. | Authors Calc. |
|---|---|---|---|---|---|---|
| 1 | Sc | | | 0.33 | 0.069±0.01 | 0.34 |
| 2 | Ti | | | 0.5 | 0.102±0.01 | 0.27 |
| 3 | $TiO_2$ | | | 0.6 | 0.183±0.027 | 0.24 |
| 4 | V | | | 0.6 | 0.163±0.016 | 0.24 |
| 5 | VO | | | | 0.250±0.025 | 0.23 |
| 6 | Cr | 0.23 | 0.26 | 0.71 | 0.234±0.023 | 0.22 |
| 7 | $Cr_2O_3$ | 0.60 | 0.39 | | 0.292±0.029 | 0.22 |
| 8 | Mn | 10.34 | 0.11 | 0.71 | 0.302±0.030 | 0.23 |
| 9 | $MnO_2$ | 0.60 | 0.14 | | 0.326±0.033 | 0.22 |
| 10 | Fe | | 0.37 | 0.66 | 0.344±0.034 | 0.22 |
| 11 | $Fe_2O_3$ | 0.71 | 0.33 | | 0.394±0.039 | 0.23 |
| 12 | Co | | | 0.6 | 0.157±0.016 | 0.21 |
| 13 | $Co_3O_4$ | | | | 0.255±0.026 | 0.22 |
| 14 | Ni | | | 0.5 | 0.112±0.020 | 0.21 |
| 15 | NiO | | | | 0.062±0.02 | 0.21 |
| 16 | Cu | | | 0.0 | 0.062±0.020 | 0.22 |
| 17 | CuO | | | | 0.063±0.02 | 0.24 |

er workers. It will be seen that the observed relative intensities of the $K\beta'$ satellite are in better agreement with our calculations than with those obtained on the basis of exchange-interaction theories. However, the data plotted in Fig. 2 suggest that in addition to the plasmon oscillation processes, probably exchange interaction may also be contributing to the origin of the low-energy $K\beta'$ satellite.

## VI. CONCLUSION

The values of the energy separation $\Delta E$ of the $K\beta'$ satellites experimentally observed by Salem *et al.*[16,17] are found to agree better with our calculated values than with the values calculated by these authors themselves on the basis of exchange-interaction theories. In the case of oxides there is no theoretically calculated data to compare with, but our calculated values agree fairly well with the observed values of Salem *et al.*[16,17] The calculated values of the relative intensity from the present theory (see Table III) also agree better with the observed values except in Sc, where the $d$ level has only one electron, and in Cu, where $d$ shell is almost completely filled. However, the data plotted in Fig. 2, suggest that possibly both plasmon oscillation and exchange interaction contribute to the origin of the $K\beta'$ satellite.

## ACKNOWLEDGMENTS

Thanks are due to Dr. B. G. Gokhale, professor and chairman of the Physics Department at Lucknow University, for helpful discussions. Thanks are also due to the University Grants Commission and the Council of Scientific and Industrial Research for their financial assistance.

*On leave from Physics Department, Hindu College Moradabad 244001, India.

[1]F. R. Hirsh, Rev. Mod. Phys. 14, 45 (1942).
[2]G. B. Deodhar, Nat. Acad. Sci. India, Annu. Number A32, 320 (1962).
[3]S. J. Edwards, Contemp. Phys. 11, 195 (1970).
[4]N. Seljakow and A. Krasnikov, Z. Phys. 33, 601 (1925); Nature (London) 117, 554 (1926).

[5]D. Coster and M. J. Druyvesteyn, Z. Phys. 40, 765 (1927).
[6]G. B. Deodhar, Proc. R. Soc. London Ser. A 131, 476 (1931).
[7]M. Sawada, Mem. Coll. Sci. Univ. Kyoto Ser. A 15, 43 (1932).
[8]M. A. Blochin, *Physik der Röntgen Strahlen* (Veb-Verlag Technik, Berlin, 1957), p. 343.
[9]K. Tsutsumi, J. Phys. Soc. Jpn. 14, 1696 (1959).
[10]L. G. Parratt, Rev. Mod. Phys. 31, 616 (1959).
[11]K. Tsutsumi and H. Nakamori, J. Phys. Soc. Jpn. 25, 1418 (1968).
[12]K. Tsutsumi, H. Nakamori, and K. Ichikawa, Phys. Rev. B 13, 929 (1976).
[13]B. Ekstig, Elisabeth Kallne, Erik Norland, and R. Manne, Phys. Scr. 2, 38 (1970).
[14]V. I. Nefedov, Izv. Akad. Nauk SSSR, Ser. Fiz. 28, 816 (1964) [Bull. Acad. Sci. USSR, Phys. Ser. 28, 724 (1964)]; J. Struct. Chem. (USSR) 5, 603 (1964); 5, 605 (1964); 7, 672 (1966).
[15]S. I. Salem, C. W. Schultz, B. A. Rabbania, and R. T. Tsutsui, Phys. Rev. Lett. 27, 477 (1971).
[16]S. I. Salem and B. L. Scott, Phys. Rev. A 9, 690 (1974).
[17]S. I. Salem, G. M. Hockney, and P. L. Lee, Phys. Rev. A 13, 330 (1976).
[18]H. W. Schnopper, Phys. Rev. 154, 118 (1967).
[19]P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1930).
[20]F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 612.
[21]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge Univ. Press, London, 1957), pp 117 and 171.
[22]J. B. Mann, Los Alamos Report No. LA-3690 (unpublished).
[23]E. Clementi, Supplement to IBM J. Res. Dev. 9, 2 (1965).
[24]T. Watanabe and C. Horie, Extended Abstract, *Proceedings of the International Conference on the Physics of X-ray Spectra* [Natl. Bur. Stand. (U.S.), Washington, D. C., 1976], p. 341.
[25]M. F. Chung and L. H. Jenkins, Surf. Sci. 26, 649 (1971).
[26]G. A. Rooke, Phys. Lett. 3, 234 (1963).
[27]J. M. Watson, R. K. Dimond, and D. J. Fables, in *Soft-X-ray Band Spectra and Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, New York, 1968), p. 45.
[28]E. T. Arakawa and M. W. Williams, Phys. Rev. B 8, 4075 (1973).
[29]D. M. Zehner, Noel Barbulesco, and L. H. Jenkins, Surf. Sci. 34, 385 (1973).
[30]L. H. Jenkins, D. M. Zehner, and M. F. Chung, Surf. Sci. 38, 327 (1973).
[31]L. H. Jenkins and D. M. Zehner, Solid State Commun. 12, 1149 (1973).
[32]L. H. Jenkins and M. F. Chung, Surf. Sci. 24, 125 (1971).
[33]L. Marton, L. B. Leder, and H. Mendlowitz, in *Advances in Electronics and Electron Physics* edited by L. Marton (Academic, New York, 1955), Vol. VII, pp. 183 and 225.
[34]C. Kittel, *Introduction to Solid State Physics*, 4th ed., 1971 (second Wiley Eastern Reprint, New Delhi, 1974), p. 227.
[35]H. Raether, Ergeb. Exakten Naturwiss. 38, 84 (1965).
[36]H. R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1530 (1963).
[37]R. C. Vehse and E. T. Arakawa, Phys. Rev. 180, 695 (1969).
[38]B. Feuerbacher and B. Fitton, Phys. Rev. Lett. 24, 499 (1970).
[39]I. B. Borovskii and V. V. Shmidt, Dok. Akad. Nauk SSSR 127, 997 (1959) [Sov. Phys.—Dokl. 4, 855 (1959)].
[40]K. S. Srivastava, J. Electron Spectros. Relat. Phenom. 20, 319 (1980).
[41]S. Glasstone, *Theoretical Chemistry* (Van Nostrand, New York, 1964), p. 97.
[42]D. C. Langreth, Phys. Rev. B 1, 471 (1970).
[43]D. C. Langreth, Phys. Rev. Lett. 26, 1229 (1971).
[44]D. C. Langreth, Noble Symp. 24, 210 (1973); *Collective Properties of Physical Systems* (Academic, New York, 1974).
[45]J. J. Chang and D. C. Langreth, Phys. Rev. B 5, 3512 (1972).
[46]G. A. Rooke, in *Soft-X-ray Band Spectra and Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, New York, 1968), p. 6.