$$A_z(\pm n) = -\frac{1}{4m\gamma(\pm n)}\left[\left(\frac{\partial^2}{\partial\mu^2} + \frac{1}{\mu}\frac{\partial}{\partial\mu} + \frac{1}{\mu^2}\frac{\partial^2}{\partial{\phi_\mu}^2} - m^2\gamma(\pm n)^2\mu^2\right) - \left(\frac{\partial^2}{\partial\nu^2} + \frac{1}{\nu}\frac{\partial}{\partial\nu} + \frac{1}{\nu^2}\frac{\partial^2}{\partial{\phi_\nu}^2} - m^2\gamma(\pm n)^2\nu^2\right)\right],$$

$$M_+(\pm n) = \frac{1}{2[m\gamma(\pm n)]^{1/2}}e^{-i\phi_\mu}\left(m\gamma(\pm n)\mu - \frac{\partial}{\partial\mu} + \frac{i}{\mu}\frac{\partial}{\partial\phi_\mu}\right)\frac{1}{2[m\gamma(\pm n)]^{1/2}}e^{-i\phi_\nu}\left(m\gamma(\pm n)\nu + \frac{\partial}{\partial\nu} - \frac{i}{\nu}\frac{\partial}{\partial\phi_\nu}\right),$$

and

$$N_-(\pm n) = -\frac{1}{2[m\gamma(\pm n)]^{1/2}}e^{i\phi_\mu}\left(m\gamma(\pm n)\mu - \frac{\partial}{\partial\mu} - \frac{i}{\mu}\frac{\partial}{\partial\phi_\mu}\right)\frac{1}{2[m\gamma(\pm n)]^{1/2}}e^{i\phi_\nu}\left(m\gamma(\pm n)\nu + \frac{\partial}{\partial\nu} + \frac{i}{\nu}\frac{\partial}{\partial\phi_\nu}\right).$$

When these operators are applied to $\psi(\pm n, j_\mu, j_\nu)$, the next formula is to be noted:

$$\phi = \phi_\mu + \phi_\nu .$$

Thus we see that the eigenvalue of $A_z(\pm n)$ is $j_\mu - j_\nu$, and $M_+(\pm n)N_-(\pm n)\psi(\pm n, j_\mu, j_\nu)$ will be just $\psi(\pm n, j_\mu + 1, j_\nu - 1)$. In these calculations, one refers to the following formulas:

$$e^{-i\theta}\left(\beta\rho - \frac{\partial}{\partial\rho} + \frac{i}{\rho}\frac{\partial}{\partial\theta}\right)e^{\pm im\theta}e^{-\beta\rho^2/2}\rho^m L^m_{m+j}(\beta\rho^2) = \begin{cases} 2(j+1)e^{i(m-1)\theta}e^{-\beta\rho^2/2}\rho^{m-1}L^{m-1}_{(m-1)+(j+1)}(\beta\rho^2) & (+) \\ -\dfrac{2\beta}{(m+j+1)}e^{-i(m+1)\theta}e^{-\beta\rho^2/2}\rho^{m+1}L^{m+1}_{m+1+j}(\beta\rho^2) & (-) \end{cases}$$

These arguments show that the value of $\frac{1}{2}A_z$ is changed from $\frac{1}{2}(j_\mu - j_\nu)$ to $\frac{1}{2}(j_\mu - j_\nu) + 1$. The energy is determined by the values n and $J = j_\mu + j_\nu$, and the degenerate bases are characterized by n and values of $J+1$ pairs which run from $(0, J)$ to $(J, 0)$. Thus for $J = 0, 1, 2, \ldots$, the irreducible representations of L_1 can be realized.

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Fine Structure of the Ti $K\beta_1\beta'$ X-Ray Emission Spectrum*

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A complex fine structure has been resolved in the $K\beta_1\beta'$ ($3p$-$1s$ transitions) x-ray emission spectrum of pure titanium metal. The measurement was performed with a double-crystal fluorescence spectrometer. The observed fine structure has been interpreted as originating from the interaction between the unpaired $3d$ electrons and the $3p$ hole in the final state of the $K\beta_1$ transition. The calculations are based on the relative energies and intensities for free-ion states of the $3p^53d^24s^2$ configuration in the Russell-Saunders coupling scheme with and without inclusion of configuration interaction. The Landé interval rule applied to these results has been found to be of minor influence on the appearance of the theoretical spectra.

In the iron transition metals with unpaired $3d$ electrons, the multiplet splitting of inner levels has been observed in x-ray photoelectron spectra[1-3] as well as in precision x-ray emission spectra.[4-8] The main advantage of x-ray emission spectroscopy (XS) over x-ray photoelectron spectroscopy (XPS) lies in the fact that x rays studied by the former method can easily penetrate the topmost surface layers of the sample. This means that XS does not suffer from effects of surface contamination such as oxidation, carbon adsorption, etc., which may distort the XPS spectra when emitted electrons are considered. Hence the information obtained in XS can be expected to come exclusively from the bulk material.

So far there have been difficulties in obtaining sufficiently high intensity and, at the same time, good energy resolution in the XS method, and therefore this method is rather seldom used in fine-structural studies of atomic levels. Recently developed precision x-ray-emission technique,[9,10] however, seems to offer a new way of approaching many interesting questions of x-ray processes in matter.

We will show in this report, for the first time, a high-resolution spectrum of $K\beta_1\beta'$ ($3p-1s$) transitions from titanium metal. The spectrum indicating several maxima reveals the complex fine structure of these transitions. It gives satisfactory support to theoretical predictions of $3p3d^2$ electrostatic interaction which should be strong enough to remove a degeneracy of the $3p$ level. As shown in the following, qualitative agreement with the experimental results is obtained if excited terms of the d^2 configuration are taken into account. Other effects, such as crystal-field splitting and $3p3d^34s$ excitations, are excluded in these calculations.

The measurements were made with a double calcite (211) crystal x-ray spectrometer with a resolving power of about 4×10^4.[10] A tungsten fluorescence tube with the power of 2.5 kW was used in excitation. The sample was 99% pure titanium powder. The experimental spectrum and the cal-

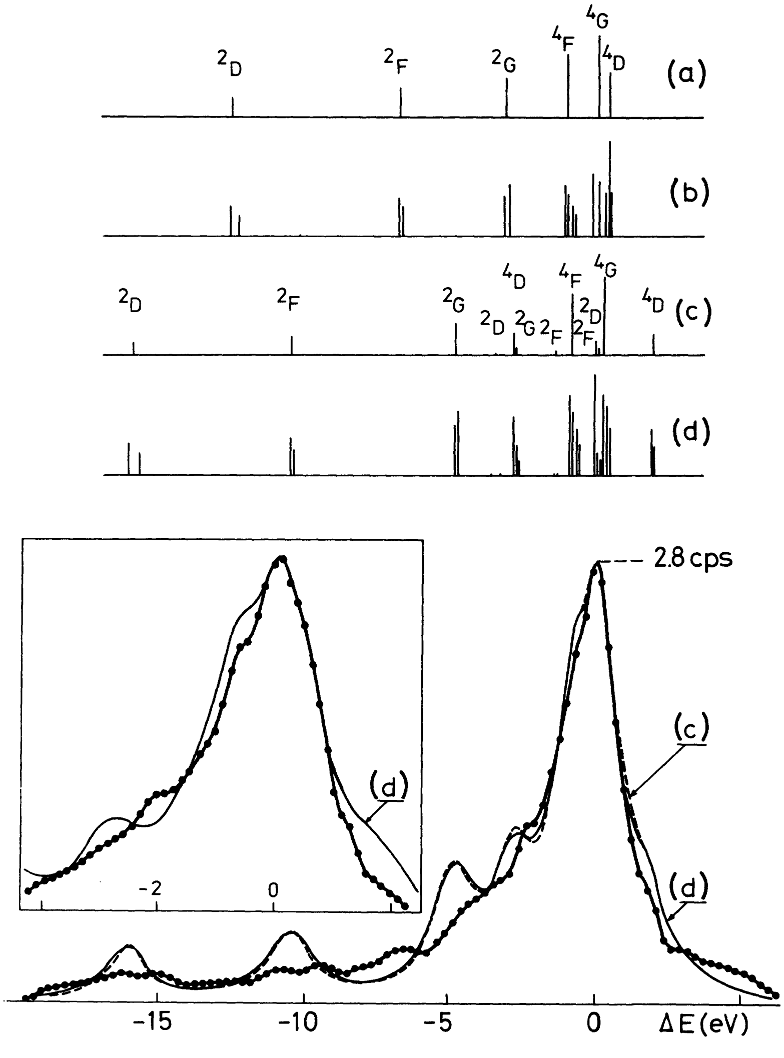

FIG. 1. Calculated line spectra (a)–(d) and the measured spectrum of Ti $K\beta_1\beta'$ from pure titanium metal. Line spectrum (a): LS coupling, configuration interaction excluded; (b) the same as (a) but the Landé interval rule applied; (c) LS coupling, configuration interaction included; (d) the same as (c) but the Landé interval rule applied. Part of the main $K\beta_1$ peak is inserted for clarity.

culated line spectra are shown in Fig. 1. Total recording time per channel was 70 min (the number of channels is 100).

The free Ti atom has a relatively simple electron configuration ($3d^2 4s^2$). It offers a favorable object for both experimental and theoretical investigations concerning the $K\beta_1\beta'$ structure. In Russell-Saunders coupling the two unpaired $3d$ electrons give rise to a ^3F spectroscopic ground state. After the $K\beta_1$ transition the six possible final states are ^4G, ^4F, ^4D, ^2G, ^2F, and ^2D. The inclusion of the excited terms of the d^2 configuration gives rise to 12 terms with possible x-ray-emission intensity. The relative energies and x-ray-emission intensities for the terms with and without configuration interaction have been calculated by Ekstig *et al.*[11] These results are shown in Fig. 1 as line spectra denoted by (c) and (a), respectively.

Provided the spin-orbit interaction can be considered as small compared to the electrostatic interaction, the splitting between different $^{2S+1}L_J$ terms can roughly be estimated using the Landé formula.[12] We have calculated the spin-orbit coupling parameters $\zeta(^{2S+1}L)$ for the terms of pd^2 configuration according to Condon and Shortley,[12] using the values $\zeta_{2p}(^2P)=0.34$ and $\zeta_{3d}(^3F)=0.03$.[6,13]

The relative intensity $I(^{2S+1}L_J)$ for a transition from a $^{2S+1}L_J$ state is proportional to the total multiplicity of this term: e.g.,

$$I(^{2S+1}L_J) \propto \frac{I(^{2S+1}L)(2J+1)}{(2L+1)(2S+1)}, \qquad (1)$$

where $I(^{2S+1}L)$ is the intensity for a transition from a ^{2S+1}L state.

The relative energies and intensities for the transition from $^{2S+1}L_J$ states calculated from the ^{2S+1}L terms with and without configuration interaction are depicted in Fig. 1 as line spectra (d) and (b), respectively. In order to simplify the comparison of line spectra (c) and (d) we have convoluted them with a Lorentzian function of FWHM = 1.5 eV. After this smearing the calculated spectra match closely with FWHM of the experimental $K\beta_1$ peak.

In the comparison of the spectra (a)–(d) with the experimental spectrum one can conclude that, concerning the relative energies, (c) and (d) give better agreement than (a) and (b). This was to be expected since configuration interaction is included in the (c) and (d) calculations. The spectra (c) and (d) differ from each other only slightly, indicating the minor influence of the Landé approximation used in the calculation of the $^{2S+1}L_J$ terms.

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