

## CALCULATED K X-RAY ABSORPTION SPECTRUM OF CALCIUM

Joseph W. McCaffrey

Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

Dimitrios A. Papaconstantopoulos

George Mason University, Fairfax, Virginia 22030, U.S.A.

(Received 26 October 1973 by A. G. Chynoweth)

The K X-ray absorption spectrum of calcium has been calculated using the results of a self-consistent energy band calculation by the augmented plane wave method. The computed spectrum is in good agreement with experiment.

THERE has been much recent interest in the various X-ray spectroscopic methods as probes of the electronic structure of materials.<sup>1</sup> The oldest and most heavily used methods, valence band emission and absorption spectroscopy, probe the partial (*s*-, *p*-, or *d*-like) densities of states because of core level angular momentum selection rules. There have been a number of calculations of the valence band emission spectra of solids, using various approximations for the valence band wave functions. For example, Goodings and Harris<sup>2</sup> and Switendick,<sup>3</sup> have expanded the valence electron wave functions in terms of augmented plane waves (APW). Recently we have applied this approach to the calculation of the X-ray absorption spectra of TiFe<sup>4</sup> and Ni<sup>5</sup>. In this paper we present a detailed calculation of the X-ray K absorption spectrum of Ca, using self-consistent eigenvalues and eigenfunctions determined by the APW energy band calculation of McCaffrey *et al.*,<sup>6</sup> which was extended by an additional 1 Ry above the Fermi level. The resulting high energy bands are shown in Fig. 1.

Within the framework of the one-electron approximation the K X-ray absorption coefficient  $\mu$  is defined by the following expression:<sup>7</sup>

$$\mu(\hbar\omega)\alpha \sum_n \int_S \frac{|M_n(\mathbf{k})|^2 dS}{|\nabla E_n(\mathbf{k})|} \quad (1)$$

where the integral is taken over the surface *S* of constant energy difference,

$$E_n(\mathbf{k}) - E_{1s} = \hbar\omega \quad (2)$$

where  $E_n(\mathbf{k})$  are the APW eigenvalues and  $E_{1s}$  the 1s core energy level. In the dipole approximation, the transition probability is given by

$$|M_n(\mathbf{k})|^2 = |\langle \psi_n(\mathbf{k}, \mathbf{r}) | \mathbf{r} | \psi_{1s}(\mathbf{r}) \rangle|^2 \quad (3)$$

where  $\psi_n$  is the wave function obtained from the self-consistent band calculation and  $\psi_{1s}$  is the 1s core wave function which was taken to be the Hartree-Fock-Slater atomic wave function.<sup>8</sup> It can be shown<sup>2</sup> that equation (3) reduces to

$$|M_n(\mathbf{k})|^2 = Q_{n,p}(\mathbf{k}) |M(1s, p\text{-like})|^2 \quad (4)$$

where  $|M(1s, p\text{-like})|^2$  is now the radial transition probability and  $Q_{n,p}(\mathbf{k})$  is the *p*-like electronic charge within the APW sphere for a given  $E_n(\mathbf{k})$ .  $Q_{n,p}$  is given by the expression:<sup>9</sup>

$$Q_{n,p}(\mathbf{k}) = \frac{\Omega}{N} \sum_i \sum_j v^*(\mathbf{k}_i) v(\mathbf{k}_j) C_{ijl} \int_0^{R_s} \left( \frac{ru_p(r, E)}{R_s u_p(R_s, E)} \right)^2 dr \quad (5)$$

where  $\Omega$  is the volume of the unit cell, *N* a normalization constant,  $C_{ijl}$  the probability of finding an electron within the APW sphere,  $v(\mathbf{k}_i)$  the eigenvectors of the APW secular equation,  $u_p$  the *p*-like radial wavefunctions and  $R_s$  the radius of the APW sphere.

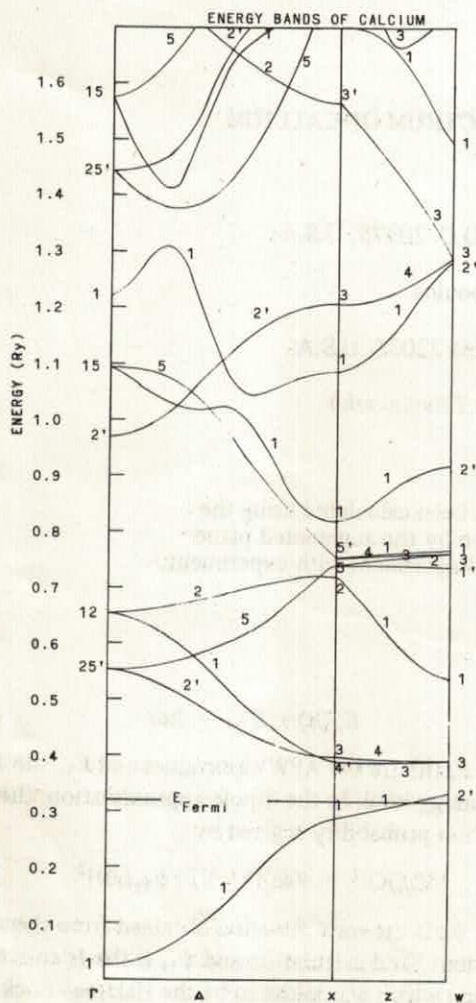


FIG. 1. The self-consistent energy bands of calcium over the region 0 to 1.7 Ry.

Substituting equations (3) and (4) into (1) one obtains

$$\mu(\hbar\omega) \propto N_p(\hbar\omega) |M(1s, p\text{-like})|^2 \quad (6)$$

where  $N_p(\hbar\omega)$  is the  $p$ -like density of states (DOS) within the APW sphere, given by:

$$N_p(\hbar\omega) = \sum_n \int_{\mathcal{S}} \frac{Q_{n,p}(\mathbf{k})}{|\nabla E_n(\mathbf{k})|} ds \quad (7)$$

and  $|M(1s, p\text{-like})|^2$  is the radial transition probability, given by:

$$|M(1s, p\text{-like})|^2 = \langle u_p(r) | r | u_{1s}(r) \rangle^2 \quad (8)$$

where  $u_p$  is the band radial wave function of  $p$  character and  $u_{1s}$  is the  $1s$  atomic wave function.

The  $p$ -like DOS is shown in Fig. 2, together with the  $s$  and  $d$ -like DOS. Those histograms were found by a Monte Carlo interpolation from the APW eigenvalues and the charges  $Q_{n,l}(\mathbf{k})$  which were calculated on a mesh of 256 points in the Brillouin zone. In Fig. 3 the radial transition probabilities to the  $1s$ ,  $2p$  and  $3p$  levels are shown. We note that the probability to the  $1s$  level, on which the  $K$  absorption spectrum depends, has a weak energy dependence.

Equation (6) was used to find the  $K$  absorption spectrum of Ca, which was then broadened by an energy dependent Lorentzian function with a width of the form

$$\gamma = (\gamma_1^2 + \gamma_2^2)^{1/2}$$

where  $\gamma_1 = 0.06$  Ry includes the spectrometer window broadening and the core broadening, and  $\gamma_2 = 0.22 (E - E_F)^2$  was the electron life time broadening.<sup>10</sup> The energy  $E$  and Fermi energy  $E_F$  were measured from the bottom of the occupied conduction band. The calculated  $K$  spectrum is shown and compared with the measurements of Sugiura<sup>11</sup> in Fig. 4. It can be seen that most of the structure in the experimental graph is also found in the calculation. The calculated peak separation is in excellent agreement with experiment although the relative heights do not agree as well. The apparent disagreement at high energies is due to the fact that the energy band calculation was truncated at 1.7 Ry. The low energy tail is due to the Lorentzian form of broadening used.

In conclusion we note [see equations (5), (6) and (7)] that the  $p$ -like DOS is strongly dependent on the wave functions, and therefore accurate wave functions are needed to perform such a calculation. On the other hand, the radial transition probability  $|M(1s, p\text{-like})|^2$  which is shown in Fig. 3 is changing only by a factor of 2 in a rather wide range of energy. Hence one may conclude that the  $K$  X-ray spectrum depends mainly on the  $p$ -like density of states. Also, in Fig. 3 we have included for comparison the  $2p$  and  $3p$  radial transition probabilities, which have stronger energy dependence. It would seem then that in calculating  $L$  and  $M$  spectra the radial transition probabilities would be more important.

*Acknowledgements* — We wish to thank D.J. Nagel for many useful discussions and acknowledge the support of the Computer Center of George Mason University.

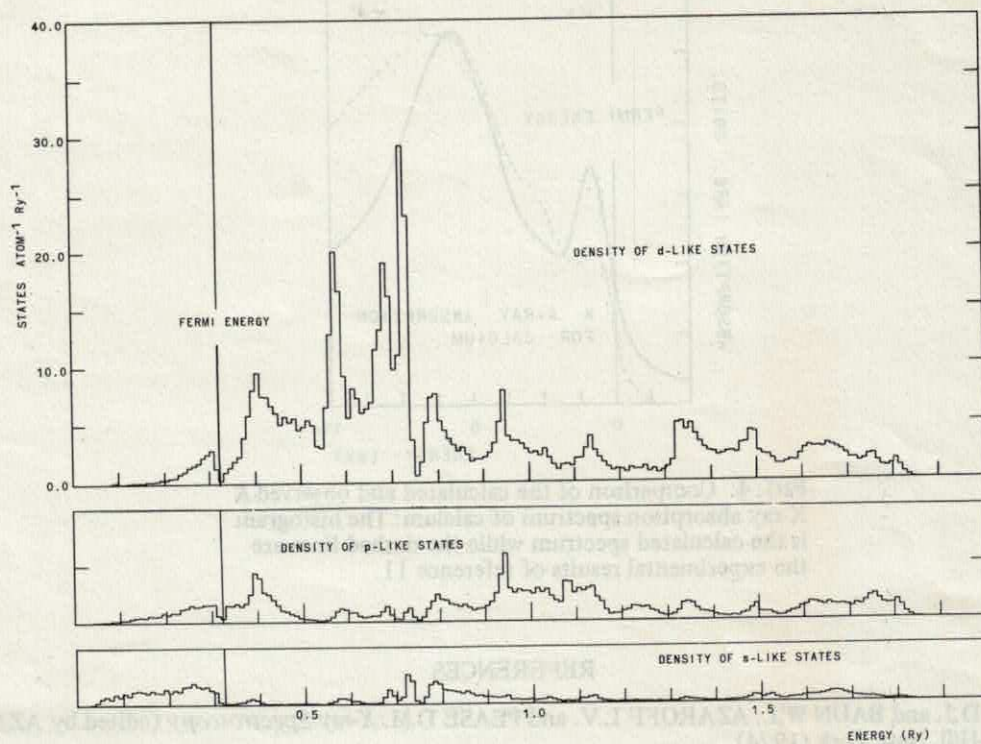


FIG. 2. The orbital densities of states of calcium within the APW sphere for  $l = 0, 1$  and  $2$ .  $K$  absorption probes the  $p$ -like character of the bands above the Fermi level.

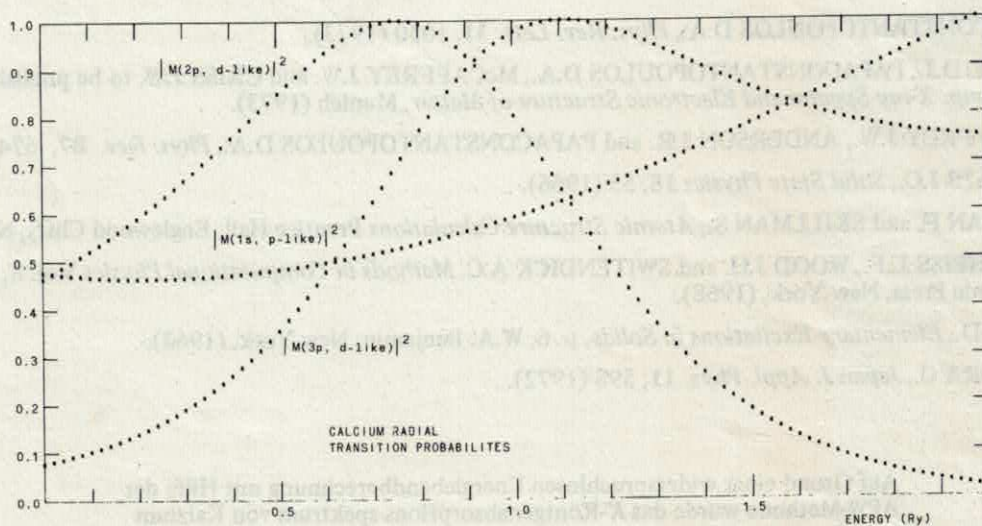


FIG. 3. Radial transition probabilities,  $|M(n, l \pm 1; l\text{-like})|^2 = \langle u_n(r) | r | u_{n, l \pm 1}(r) \rangle^2$

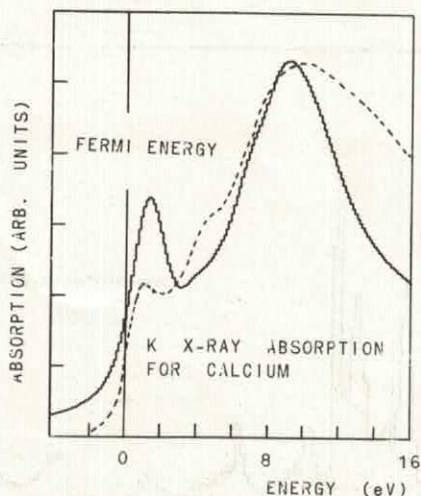


FIG. 4. Comparison of the calculated and observed K X-ray absorption spectrum of calcium. The histogram is the calculated spectrum while the dashed lines are the experimental results of reference 11.

#### REFERENCES

1. NAGEL D.J. and BAUN W.L. AZAROFF L.V. and PEASE D.M. *X-ray Spectroscopy* (edited by AZAROFF L.V.) McGraw-Hill, New York (1974).
2. GOODINGS D.A. and HARRIS R., *J. Phys. C*, 2, 1808 (1969).
3. SWITENDICK A.C. *Electronic Density of States*, p. 297, NBS Spec. Publ. No. 323 U. S. Printing Office, Washington, (1971).
4. PAPACONSTANTOPOULOS D.A., *Phys. Rev. Lett.* 31, 1050 (1973).
5. NAGEL D.J., PAPACONSTANTOPOULOS D.A., McCAFFREY J.W. and CRISS J.W. to be published in *Proc. Int. Symp. X-ray Spectra and Electronic Structure of Matter*, Munich (1973).
6. McCAFFREY J.W., ANDERSON J.R. and PAPACONSTANTOPOULOS D.A., *Phys. Rev.* B7, 674 (1973).
7. PHILLIPS J.C., *Solid State Physics* 18, 55 (1966).
8. HERMAN F. and SKILLMAN S., *Atomic Structure Calculations* Prentice-Hall, Englewood Cliffs, N. J. (1963).
9. MATTHEISS L.F., WOOD J.H. and SWITENDICK A.C. *Methods in Computational Physics* Vol. 8, p. 123, Academic Press, New York, (1968).
10. PINES D., *Elementary Excitations in Solids*, p. 6. W.A. Benjamin, New York, (1963).
11. SUGIURA C., *Japan J. Appl. Phys.* 11, 598 (1972).

Auf Grund einer widerspruchlosen Energiebandberechnung mit Hilfe der APW-Methode wurde das K-Röntgenabsorptionsspektrum von Kalzium berechnet. Die Ergebnisse stimmen mit experimentellen Werten gut überein.