1

OFFICE OF NAVAL RESEARCH
GRANT N00014-94-I-0331

R & T Code 4133044
Robert Nowak

Technical Report No. 68

Two-Center, Two Electron Excitations Identified in NEXAFS for Solid Ne

by

H. Sambe, X. Qian and D.E. Ramaker

Prepared for Publication

in

Physics Review Letters

George Washington University
Department of Chemistry
Washington, D.C.

September 1994

28

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE September 1994	3. REPORT TYPE AND DATES COVERED Technical Sept'93-Oct'94

4. TITLE AND SUBTITLE
Two-Center, Two-Electron Excitations Identified in NEXAFS for Solid Ne

5. FUNDING NUMBERS
Grant #:
N00014-93-I-0331
Robert Nowak, Prog Off
R & T: 4133044

6. AUTHOR(S)
H. Sambe, X. Qian, and D.E. Ramaker

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Chemistry Department
George Washington University
Washington, D.C. 20052

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
#68

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE
Approved for public release and sale; distribution is unlimited

13. ABSTRACT *(Maximum 200 words)*

Experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne are compared with theoretical results. Seven features in the experimental spectrum that are not reproduced by the theoretical results are found to be attributable to two-electron excitations. Five of them are usual *one-center* excitations, but the remaining two are found to be novel *two-center* excitations involving resonant orbitals as opposed to the usual bound orbitals. In contrast, *two-center, two-electron* excitations involving only bound orbitals are found to be absent in the experimental spectrum.

14. SUBJECT TERMS
Rare Gases, X-Ray Absorption, NEXAFS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

Two-center, Two-electron Excitations Identified in NEXAFS for Solid Ne

H. Sambe, X. Qian, and D.E. Ramaker

Chemistry Department, George Washington University, Washington, D. C. 20052

Experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne are compared with theoretical results. Seven features in the experimental spectrum that are not reproduced by the theoretical results are found to be attributable to two-electron excitations. Five of them are usual *one-center* excitations, but the remaining two are found to be novel *two-center* excitations involving resonant orbitals as opposed to the usual bound orbitals. In contrast, *two-center, two-electron* excitations involving only bound orbitals are found to be absent in the experimental spectrum.

PACS numbers: 78.70.Dm, 32.30.Rj, 71.90.+q

In photo-absorption spectra, one-electron (*1-e*) excitations normally dominate the spectra for obvious reasons. Much weaker two-electron (*2-e*) shakeup excitations, nevertheless, have been observed in many atomic, molecular, and solid systems. In solids and molecules, these *2-e* excitations can be either one-center (*1-c*) or two-center (*2-c*), i.e., two holes can be located at the same or different atoms. Most of the observed *2-e* excitations are *1-c*. Only a few *2-c* excitations have been identified, for example, in alkali halides [1], $PrCl_3$ crystal [2], $(O_2)_2$ dimers isolated in solid Ne [3], and Ar solid [4]. All of these observed *2-c* excitations are associated with two identical valence excitations (except that of Ref. [2] which involves different valence excitations) and are observed in the UV region well below 30eV. This begs the question: Are *2-c* excitations restricted to valence excitations, when strong mutual interactions are guaranteed due to the large hole size and similar excitation energies? In this Letter, we shall identify, for the first time, *2-c* excitations involving a core excitation in the X-ray region. Another novel aspect of the identified *2-c*, *2-e* excitations is involvement of resonant rather than bound orbitals, i.e., quasi-stationary orbitals in the continuum.

Figure 1 compares experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne with our theoretical results. The experimental data were recently measured by Hiraya et al. [5] with high energy resolution (0.46eV) for a thick Ne film condensed at 6.3K. A dramatic "thickness effect" is observed for the sharpest peak, E_1. To reduce this effect, Hiraya et al. also measured spectra on thin Ne films, which illustrated that the E_1 peak intensity is about eight times stronger than the R_2 peak intensity, contrary to Fig. 1: The E_1 peak actually dominates the spectrum. Our theoretical results are calculated utilizing a curved-wave, multiple-scattering (MS) approach (FEFF6) recently developed by Rehr and co-workers [6,7]. The input data for these calculations include the coordinates for 87 atoms (which form 6 shells with an fcc lattice constant of 4.463Å [8]), the sample temperature (6.3K), the Debye temperature (66.0K) [9], and a choice for the self-energy as described below. All other information, including the core lifetime, are internally provided by the code. We have performed full MS calculations incorporating the maximum number of paths that the code allows. In Ne solid, the inelastic mean free path of the photoelectrons is very long (>80Å) for electron energies less than 20eV but rapidly decreases to 20Å above 30eV [10]. In order to include this large variation in the mean free path, we have performed two calculations, one without inelastic loss [theory (a)] and one with inelastic loss [theory (b)]. We employed the ground-state, exchange-correlation potential with a zero imaginary part for (a) and the complex Hedin-Lundquist self-energy for (b). Thus, the theoretical result (a) simulates the experimental spectrum below 30eV and (b), above 30eV. These sections of the spectra are indicated by solid lines in Fig. 1 and represent our theoretical spectrum.

The sharpest peak (E_1) in the experimental solid Ne spectrum closely resembles the $1s \rightarrow 3p$ excitation peak for gaseous Ne, so that peak E_1 has been attributed to the $1s \rightarrow 3p$ exciton [5]. The FEFF6 model is limited to an "extended" continuum spectrum above the Fermi level, and hence excitonic peaks are not well reproduced with this model [6]. A small kink near the threshold in the theoretical spectrum does suggest a trace of the $1s \rightarrow 3p$ exciton. Peaks R_i for i=1-8 in the experimental spectrum, which are well reproduced by the theoretical spectrum, are attributable to *1-e* excitations, $1s \rightarrow \varepsilon_i p$, where $\varepsilon_i p$ are resonant orbitals arising from scattering interference. The experimental features that are not reproduced by the theoretical spectrum are shaded in the figure and labeled D_i for i=1-7. Below we shall discuss the origins of those D_i features.

The structure comprising the D_3-D_5 features is virtually identical to the structure observed in the NEXAFS of gaseous Ne [11] except for a uniform shift of 1.8eV to higher energy. This structure in the gas phase has been attributed to ^1P states arising from the $1s^1 2s^2 2p^5 3p^2$ configuration, final states in the $1s2p \rightarrow 3p3p$ excitation. These localized *2-e* excitations are expected to survive in the solid phase, just as the $1s \rightarrow 3p$ excitation does, so the D_3-D_5 features can be attributed to those ^1P states [12]. Similarly, we can show that the

D_6 and D_7 peaks are due to two ^1P states resulting from the $1s2s \rightarrow 3s3p$ excitation. The separation between the two ^1P states is large, because they are almost pure states of $[(1s2s)^3S(3s3p)^3P]^1P$ and $[(1s2s)^1S(3s3p)^1P]^1P$ and the $2s$ orbital is substantially relaxed due to creation of the 1s hole. All of these assignments involving *1-c, 2-e* excitations will be discussed and justified in detail elsewhere [13] together with similar *1-c, 2-e* excitations observed in Ar and Kr solids.

The D_1 and D_2 features are enlarged and shown in Fig. 2. Removing a smooth background with straight lines in two reasonable ways, the D_1 and D_2 contributions are isolated. Their peak energies are found to be insensitive to the background removal procedure. These contributions cannot be due to *1-c, 2-e* excitations, because the lowest *1-c, 2-e* excitation (i.e., $1s2p \rightarrow 3s3s$) is well above 900eV [13]. They must be due to *2-c, 2-e* excitations of the monopole shakeup type, such as the $1s_a \rightarrow 3p_a$ dipole excitation accompanied with monopole excitation $2p_b \rightarrow 3p_b$ or $2p_b \rightarrow \varepsilon_i p_b$, where the subscripts *a* and *b* denote different atomic centers. Alternative excitations, the $1s_a \rightarrow \varepsilon_i p_a$ dipole excitations accompanied with the $2p_b \rightarrow 3p_b$ monopole excitation, should be much weaker than the above-mentioned excitations, because the R_i intensities due to the $1s_a \rightarrow \varepsilon_i p_a$ excitations are much weaker than the E_1 intensity due to the $1s_a \rightarrow 3p_a$ excitation. Recall that the E_1 peak actually dominates the absorption spectrum. Thus, the probable excitations for the D1 and D2 contributions are $1s_a 2p_b \rightarrow 3p_a 3p_b$ or $1s_a 2p_b \rightarrow 3p_a \varepsilon_i p_b$.

The energies of these probable *2-c, 2-e* excitations are approximately given by the $1s_a \rightarrow 3p_a$ excitation energy (i.e., the E_1 peak energy) plus the $2p_b \rightarrow 3p_b$ or $2p_b \rightarrow \varepsilon_i p_b$ excitation energy on a neighboring Ne atom. The $2p \rightarrow 3p$ excitation energy in solid Ne is, in a very good approximation, equal to that (18.5eV [14]) in the gas phase plus the "solid-state" shift ($\approx$1.2eV [5]) due to the Pauli repulsion of the 3p electron by the neighboring Ne atoms. Further, the difference between the $2p \rightarrow 3p$ and $2p \rightarrow \varepsilon_i p$ excitation energies should be approximately equal the energy separation between the $E_1(1s \rightarrow 3p)$ and $R_i(1s \rightarrow \varepsilon_i p)$ features in Fig. 1. (In fact, a more detailed spectrum [5] than that in Fig. 1 was used for these energy separations.) The estimated energies of the probable excitations are included in Fig. 2, which suggests that the $1s_a2p_b \rightarrow 3p_a\varepsilon_ip_b$ excitation energies for $i=1$ and 2 agree with the D_1 and D_2 peak energies except for a uniform downward shift of about 1.4eV. One can attribute this downward shift to the Coulomb attraction between the positive $1s_a$ hole and an electron that occupies the ε_ip_b orbital, $U(1s_a, \varepsilon_ip_b)$, which has not been included in the theoretical estimates. This agreement on the energies suggests that the D_1 and D_2 contributions are due to the $1s_a2p_b \rightarrow 3p_a\varepsilon_ip_b$ excitations for $i=1$ and 2, respectively.

Figure 2 also shows that the *2-c, 2-e* shakeup process is selective, because the $1s_a2p_b \rightarrow 3p_a3p_b$ and $1s_a2p_b \rightarrow 3p_a\varepsilon_3p_b$ excitations are apparently absent in the experimental spectrum. One can explain the absence of the localized excitation $1s_a2p_b \rightarrow 3p_a3p_b$ by invoking a well-known shakeup mechanism. That is, a shakeup peak appears only when the orbitals relax upon creation of a hole, so that the monopole overlap integral does not vanish, (i.e., $\langle 2p_b | 3p_b' \rangle$ in the present case, where the prime indicates a relaxed orbital of the excited state). In the $1s_a^{-1}2p_b^{-1}3p_a3p_b$ excited state, however, the *2-c* attraction $U(1s_a, 3p_b)$ is negligible, because the $1s_a$ core hole is shielded by the $3p_a$ electron from the view point of an electron in the $3p_b$ orbital localized around another atomic center. On the other hand, the more delocalized ε_1p_b and ε_2p_b resonant orbitals do sense the attractive potential as revealed by the 1.4eV downward shift already mentioned above, i.e., $U(1s_a, \varepsilon_ip_b) \approx 1.4\text{eV}$ for $i=1$ and 2. The lower-energy resonant orbitals ε_ip_b for $i=1$ and 2 apparently penetrate into the atomic region of center *a*, but the higher energy orbitals for $i \geq 3$ are expected to stay outside of the atomic regions. More importantly, additional nodal planes in the higher-energy orbitals tend to make the overlap integral, $\langle 2p_b | \varepsilon_ip_b' \rangle$, much smaller. These trends can account for the absence of the $1s_a2p_b \rightarrow 3p_a\varepsilon_3p_b$ and higher *2-c, 2-e* excitations.

In conclusion, one can attribute the D_1 and D_2 contributions to the $1s_a2p_b \rightarrow 3p_a\varepsilon_ip_b$ monopole-shakeup excitations for $i=1$ and 2, respectively. The relaxation of the delocalized resonant orbitals $\varepsilon_i p_b$ upon creation of the $1s_a$ core hole is responsible for the appearance of these *2-c* shakeup excitations. It should be noted that these excitations involve a resonant orbital $\varepsilon_i p$ embedded in the continuum, unlike commonly known *2-e* shakeup mechanisms that involve only bound orbitals. If $\varepsilon_i p$ were completely delocalized in the continuum, on the other hand, the *2-e* excitations would represent the normal shakeoff process; these features appear step-like or disappear into the background in absorption spectra. Thus, the *2-e* excitations identified here are novel, for they involve not only two centers but also resonant orbitals. To our knowledge, this is the first identification of *2-c* shakeup excitations involving a core hole.

This work was supported by the U.S. Office of Naval Research.

References

[1] J.T. Devreese, A.B. Kunz, and T.C. Collins, Solid State Comm. **11**, 673 (1972).

[2] F. Varsanyi and G.H. Dieke, Phys. Rev. Lett. 7, 442 (1961).

[3] J. Goodman and L.E. Brus, J. Chem. Phys. **67**, 4398 (1977).

[4] Y. Baba, G. Dujardin, P. Feulner, and D. Menzel, Phys. Rev. Lett. **66**, 3269 (1991); T. Schwabenthan, R. Scheuerer, E. Hudel, and P. Feulner, Solid State Comm. **80**, 773 (1991).

[5] A. Hiraya, K. Fukui, P.-K. Tseng, T. Murata, and M. Watanabe, J. Phys. Soc. Jpn. **60**, 1824 (1991).

[6] J. Mustre de Leon, J.J. Rehr, S.I. Zabinsky, and R.C. Albers, Phys. Rev. **B 44**, 4146 (1991).

[7] J.J. Rehr, Jpn. J. Appl. Phys. Suppliment **32**, 8 (1993).

[8] G.K. Horton, Am. J. Phys. **36**, 93 (1968).

[9] H.R. Glyde, in *Rare Gas Solids*, edited by M.L. Klein and J.A. Venables (Academic, London, 1976), p. 382.

[10] See for example, N. Schwentner, E.-E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases* (Springer-Verlag, Berlin, 1985), p. 199.

[11] J.M. Esteva, B. Gauthe, P. Dhez, and R.C. Karnatak, J. Phys. **B 16**, L263 (1983).

[12] Recently Soldatov et al. [A. V. Soldatov, T.S. Ivanchenko, S.D. Longa, and A. Bianconi, Phys. Rev. **B 47**, 16155] attributed the D_3 and D_4 features to $1s2p \rightarrow 3p3p$ and $1s2p \rightarrow \varepsilon_1 p \varepsilon_1 p$ excitations, respectively, based on the similarity between the (D_3, D_4) and (E_1, R_1) energy separations, which we reject.

[13] H. Sambe, X. Qian, and D.E. Ramaker (to be published).

[14] C.E. Moore, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) **35**, 359 (1971).

Figure Captions

Fig. 1. Comparison of experimental K-edge NEXAFS for solid Ne with theoretical results. Solid lines of theory (a) and (b) represent our theoretical spectrum as described in the text. The experimental spectrum is interpreted as follows: E_1 is an *excitonic* excitation; R_1-R_8 are *one-electron* excitations; D_3-D_7 are *one-center, two-electron* excitations; and D_1-D_2 are *two-center, two-electron* excitations.

Fig. 2. Experimental spectrum (Fig. 1) in the 880-900 eV range. The D_1 and D_2 contributions are isolated from the spectrum by removing a smooth background using straight lines in two reasonable ways. Solid bars represent predicted energy positions for $1s_a2p_b \rightarrow 3p_a3p_b$ ($3p$) and $1s_a2p_b \rightarrow 3p_a\varepsilon_i p_b$ ($\varepsilon_i p$) excitations.

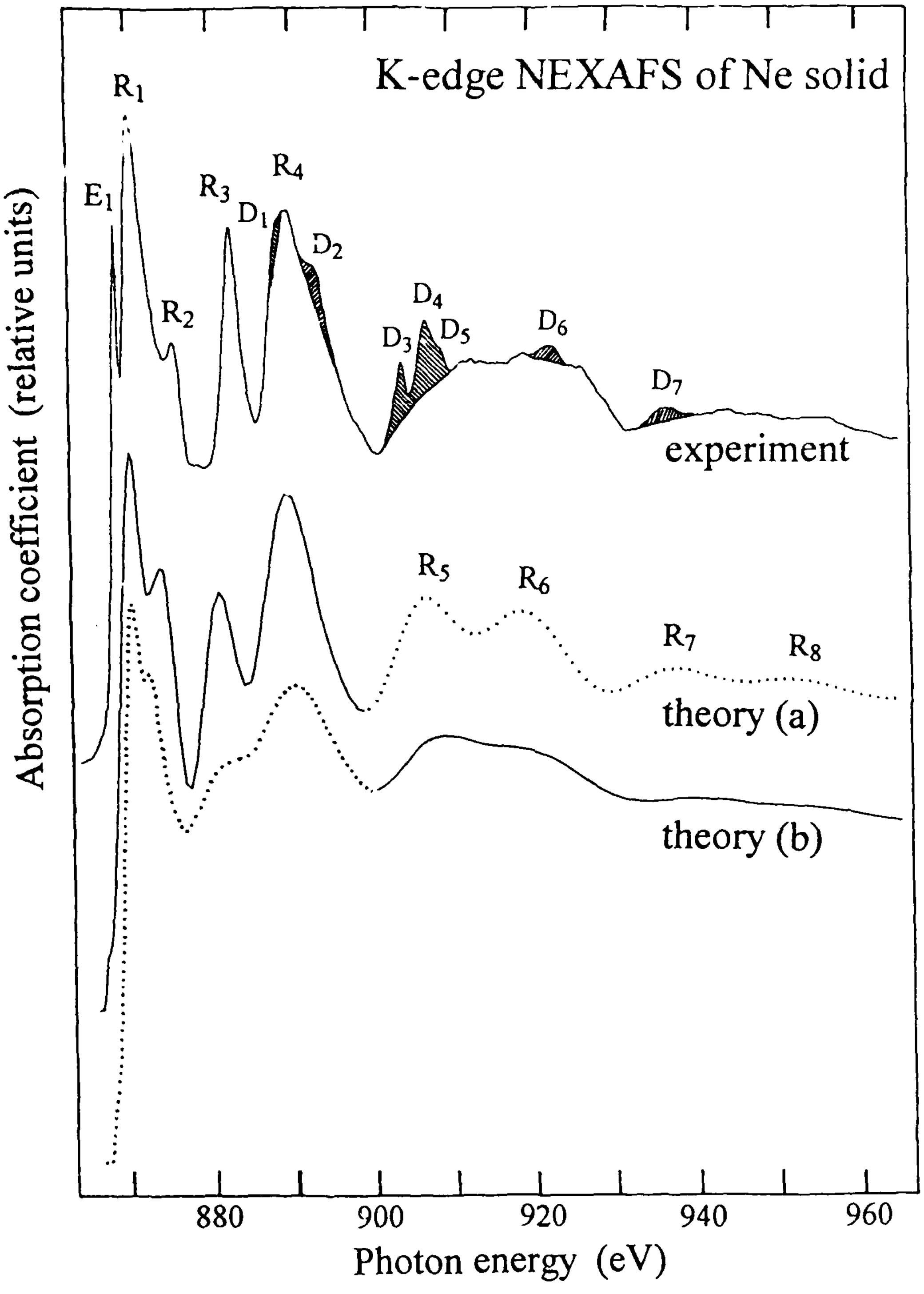
K-edge NEXAFS of Ne solid
R1
E1
R2
R3
D1
R4
D2
D3
D4
D5
D6
D7
experiment
R5
R6
R7
R8
theory (a)
theory (b)
Absorption coefficient (relative units)
880
900
920
940
960
Photon energy (eV)

Fig. 1

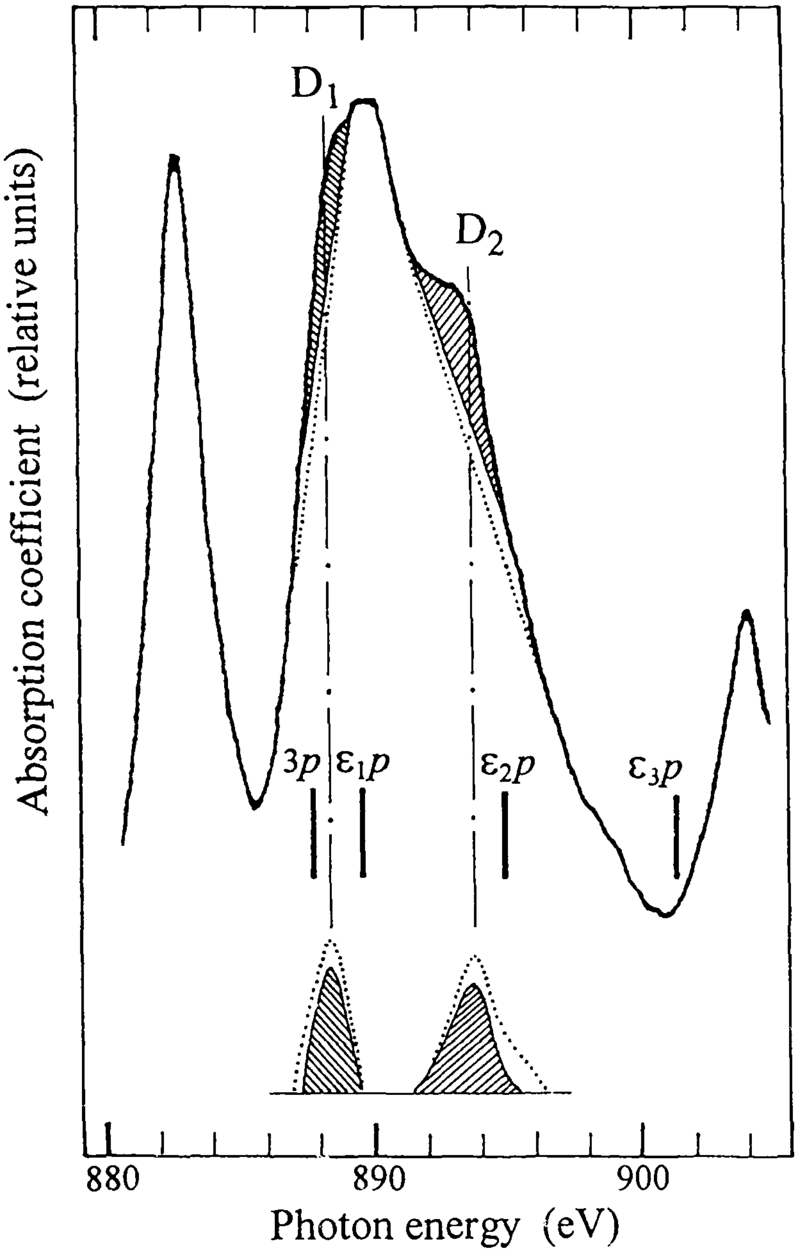
D1
D2
3p
ε1p
ε2p
ε3p
880
890
900
Photon energy (eV)
Absorption coefficient (relative units)

Fig. 2