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[1]See the following review articles and references therein: D. F. Measday and G. A. Miller, Annu. Rev. Nucl. Sci. 29, 121 (1979); H. W. Fearing, in "Progress in Particle and Nuclear Physics," edited by D. Wilkinson (Pergamon, New York, to be published).

[2]M. Tsangarides, Ph.D. thesis, Indiana University, 1979 (unpublished), and Indiana University Cyclotron Facility Report No. 79-4 (unpublished).

[3]R. Brockmann and M. Dillig, Phys. Rev. C 15, 361 (1977).

[4]L. D. Miller and H. J. Weber, Phys. Lett. 64B, 279 (1976).

[5]L. D. Miller and H. J. Weber, Phys. Rev. C 17, 219 (1978).

[6]R. Brockmann, Phys. Rev. C 18, 1510 (1978).

[7]L. D. Miller and A. E. S. Green, Phys. Rev. C 5, 241 (1972).

[8]L. G. Arnold, B. C. Clark, and R. L. Mercer, Phys. Rev. C 19, 917 (1979).

[9]J. D. Walecka, Ann. Phys. (N.Y.) 83, 491 (1974).

[10]E. D. Cooper, Ph.D. thesis, University of Alberta, 1981 (unpublished).

[11]E. D. Cooper and H. S. Sherif, to be published.

[12]K. Stricker, H. McManus, and J. A. Carr, Phys. Rev. C 19, 929 (1979).

[13]J. L. Friar, Phys. Rev. C 15, 1783 (1977).

[14]J. V. Noble, Phys. Rev. Lett. 43, 100 (1979).

[15]M. Gell-Mann and M. Lévy, Nuovo Cimento 16, 705 (1960).

[16]P. H. Pile, R. D. Bent, R. E. Pollock, P. T. Debevec, R. E. Marrs, M. C. Green, T. P. Sjoreen, and F. Soga, Phys. Rev. Lett. 42, 1461 (1979).

[17]P. M. Endt and C. van der Leun, Nucl. Phys. A310, 1 (1978).

[18]P. H. Pile, T. P. Sjoreen, R. D. Bent, M. C. Green, and F. Soya, Indiana University Cyclotron Facility Scientific and Technical Report No. 62, 1979 (unpublished).

[19]E. G. Auld, A. Haynes, R. R. Johnson, G. Jones, T. Masterson, E. L. Mathie, D. Ottewell, and P. Walden, Phys. Rev. Lett. 41, 462 (1978).

[20]G. A. Miller, Nucl. Phys. A224, 269 (1974).

[21]T. P. Sjoreen, P. H. Pile, R. E. Pollock, W. W. Jacobs, H. O. Meyer, R. D. Bent, M. C. Green, and F. Soga, Phys. Rev. C 24, 1135 (1981).

Measurement of Subshell Photoionization Cross Sections of Ba near the 4*d* Threshold

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Measurements of 4*d*, 5*p*, and 5*s* subshell cross sections have been performed on polycrystalline Ba. These results essentially confirm many-body atomic calculations including the resonant enhancement of photoemission from the outer shells at the 4*d* threshold. Evidence is also presented for a two-electron discrete excited state about 20 eV above the 4*d* threshold.

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We present here measurements of the angle-integrated 5*p*, 5*s*, and 4*d* subshell photoionization cross sections for polycrystalline Ba around and above the 4*d* threshold. Soft-x-ray–induced photoemission in Ba is dominated by many-electron interactions: A broad 4*d* resonance is accompanied by outer-shell photoexcitation resonances near the threshold which cannot be explained in the framework of a one-electron model.

The energy of soft x rays absorbed in a solid or gas is converted principally into photoelectron energy. The kinetic energy of outgoing photoelectrons provides information about the initial and final states of the atomic excitation responsible for the absorption. The experiment described here employs an electron energy analyzer in conjunction with a tunable soft x-ray source, so that we are thus able to determine the partition of the absorption into several types of excitations. Previous experiments on similar systems have measured only total cross section—the total attenuation of a photon beam through a thin film or gas sample.

Measurements of subshell cross sections in the solid state is experimentally much simpler than in the gas phase (although interpretation of the

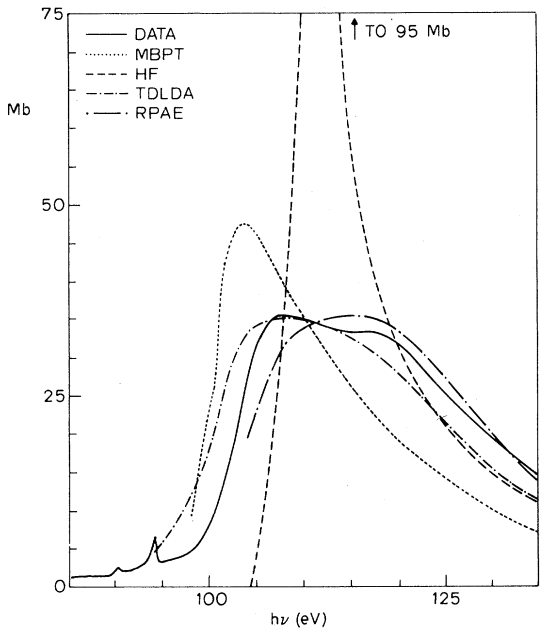

FIG. 1. Total Ba 4*d* cross section compared to several calculations by various authors: generalized random phase approximation with exchange (GRPAE) (Ref. 1), many-body perturbation theory (Ref. 3), time-dependent local density approximation (Ref. 4), and Hartree-Fock (Ref. 5). The data have been normalized to the peak of the GRPAE calculation.

data is more difficult). Such measurements are also of great interest in their own right as a way of shedding light on the role of localized excitations in the solid.

Absorption spectra of solids and gases are generally similar except for a smearing out of detail in the solid. This is not surprising for deep core levels or narrow bands when electrons are excited far above the Fermi level. Ba provides an interesting test of the limits of applicability of this atomiclike excitation model, since the details of the 4*d* excitation are critically dependent on unoccupied levels just above the Fermi level. Only with photoemission can these details be studied.

4*d* excitations in Xe-like atoms are of particular theoretical interest because under certain circumstances there can be a large overlap of the 4*d* electron with the final-state *f*-type wave function as a result of many-electron effects. The importance of the Ba system as a test of many-body theory is underscored by the fact that the 4*d* cross section alone has been the subject of at least eighteen different calculations by five sets of authors in recent literature[1-5] (Fig. 1). Only the most sophisticated of these calculations have been able to adequately describe previously measured absorption spectra.[6,7]

The measurements were all performed on the 4-deg beam line of the Stanford Synchrotron Radiation Laboratory (SSRL).[8] The samples were prepared by *in situ* evaporation in an ultrahigh vacuum environment. The monochromator transmission was determined by using a calibrated photodiode, by measuring the photoyield for Au,[9] and by using a numerical method to remove contributions from nonmonochromatic light. The cylindrical mirror analyzer was run in a constant retarding ratio ($\Delta E/E = \text{const}$) mode to take advantage of the resulting constant transmission function.[10] The sample normal was oriented at less than 30 deg from the light beam to avoid reflection and refraction from the sample surface. The area under each photoemission peak of interest was then measured as a function of photon energy.[11]

No correction was made for direct two-electron continuum emission under the assumption that high ionization states are more easily reached by photoemission and subsequent Auger decay. Satellite structure, which is a small fraction of the total emission, was included in the photoemission peak when possible. It should be noted that neither of these effects would reduce the rate of Auger decay of the 4*d* hole.

The Auger electron yield, which should be proportional to the rate of core hole creation (and thus, in most cases, the photoelectron yield), was similarly measured. The total absorption cross section was measured using the partial-yield technique, i.e., by measuring the yield of low-energy electrons as a function of photon energy. Both Auger and partial-yield measurements were corrected for contributions from harmonics of the fundamental photon energy. The results are extremely sensitive to corrections for electron-kinetic-energy–dependent effects, i.e., escape depth,[12] surface refraction (which narrows the escape cone), and surface reflection of electrons.[13] Justification of the corrections applied will be presented in a future publication.

Evidence for the localized nature of the 4*d* excitation is provided by Rabe's absorption measurements on Ba vapor and films, which are similar in all but the details of the fine structure, which are smeared out for the solid.[6] Our photoelectron-yield data (Fig. 2) were indistinguishable from Rabe's thin-film absorption data except for a sloping background which we did not observe.

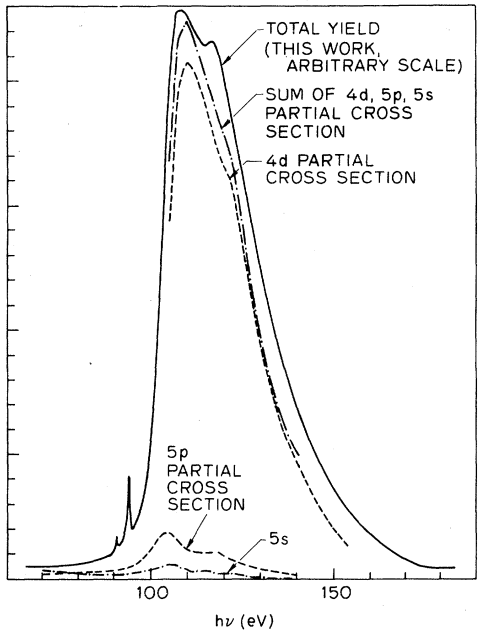

FIG. 2. Total yield, partial cross sections, and sum of partial cross sections of Ba (this work).

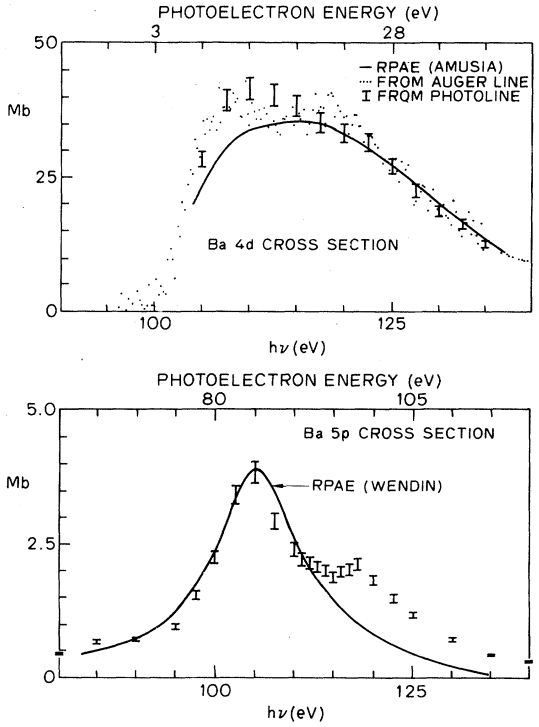

FIG. 3. $4d$ and $5p$ partial cross sections of Ba compared to RPAE and GRPAE calculations (Refs. 1 and 16). The $4d$ cross section is normalized to the calculation at 125 eV.

The photoemission results are displayed in Fig. 3. The absolute cross sections were assigned by fitting the tail of the $4d$ cross section with the theoretical curve. The error bars refer to statistical errors only. The $4d$ partial cross section (Fig. 3) has been determined both by a measurement of the direct photoemission line and the associated Auger decay lines.

The broad, delayed onset of the $4d$ emission can be described as the result of a centrifugal barrier which can confine the f-type wave functions and thus produce a large overlap with the $4d$ hole.[14] Somewhere between Xe and La, depending upon the details of the atomic configuration, the final-state wave function collapses into the inner potential well. Chiang *et al.*[15] have suggested that this collapse occurs for Cs and heavier elements, based on an analysis of the $N_{45}O_{23}$-O_{23} line shape. (Connerade notes that this collapse is extremely sensitive to excited atomic configurations,[14] a fact that should be considered in interpreting the solid-state results.)

The final state of the $4d$ excitation is a continuum wave function which closely resembles a $4f$ wave function inside the potential barrier.[14,16] Connerade[14] has therefore denoted this wave function $\overline{4, \epsilon f}$. (There has been some confusion about the identification of this level, which has been resolved by the finding that all the nf wave functions lose a node upon collapse.[14,16])

The enhancement of the outer shells at the $4d$ threshold is usually described[2] as an autoionization phenomenon resulting from a process such as

$$4d^{10}5s^25p^6 \rightarrow 4d^95s^25p^6\overline{4, \epsilon f} \rightarrow \begin{cases} 4d^{10}5s^25p^5 + e^- \\ 4d^{10}5s^15p^6 + e^- \end{cases}$$

interfering with the direct outer-shell photoemission. This is in analogy to the decay of a discrete Rydberg state, in which case the resulting profile would be described by the simple Fano interference formalism.[17] Since this intermediate state is, in fact, a continuum level, it is more rigorous to describe the enhancement as purely an interchannel coupling effect caused by the induced dipole field at the $4d \rightarrow \overline{4, \epsilon f}$ threshold.[4]

The feature at about 120 eV in the total cross section and in the $5p$ and $5s$ subshell cross sections of Ba is not adequately described by any of the theoretical models, and is probably due to a final state involving a $4d$ and a $5p$ hole, according to the excitation

$$4d^{10}5s^25p^6 \rightarrow 4d^95s^25p^5nln'l'.$$

Wendin[18] has suggested $nln'l'=(5d5d)$, although other configurations such as $(6p4f)$ are also allowed. The associated outer-shell enhancements are further evidence of the discrete nature of this intermediate state. We suggest that the enhancement in the $N_{45}O_{23}O_{23}$ Auger line and in the $5p$ cross section is due to a decay of this excited state to a $(4d^{10}5p^4)$ and $(4d^{10}5p^5)$ configuration, respectively. It cannot be determined from the data whether a similar enhancement can be seen in the $4d$ photoemission yield.

These results are different from similar measurements for vapor-phase xenon by West *et al.*[19] and Adam *et al.*[20,21] in two noteworthy ways. The Xe measurements showed no such structure from two-electron excitation. In addition, the peaks of the $4d$, $5p$, and $5s$ cross section were quite a bit closer in energy than in the present measurements. Thus it appears that the coupling in Ba is significantly more complex than in Xe, perhaps as a result of the collapse of the $4f$ level in Ba.

It can be seen in Fig. 2 that the sum of the $5p$ and $4d$ partial cross sections closely resembles the total cross section as measured with constant final-state spectroscopy. In addition, except for the secondary peak at 120 eV, the shapes of the subshell cross sections are in good agreement with the theoretical curves of Wendin.[2,18]

It is clear that photoexcitation in Ba is extremely complex, resulting in significant rearrangement of the initial-state atom and a variety of interacting excitation and decay channels. This measurement demonstrates that advanced many-body techniques such as the RPAE can reproduce general trends of the principal $4d$ excitation as well as the outer-shell enhanced excitation. The details of multielectron excitation are, however, important and have not as yet been adequately calculated.

It is, in addition, clear that the details of the excitation in the solid are both qualitatively and quantitatively consistent with a totally atomic description. Thus it would appear that, at least in elemental metals, we are justified in using atomic models for excitation of levels which are corelike or localized in the initial state. Evidence is still scarce about the extent to which formation of compounds affects the excitation: We suggest such a study as a fruitful extension of the present work. Finally we note that the study of photoemission in solids appears to hold promise for determining precisely the value of subshell cross sections and related quantities.

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[1]M. Ya. Amusia, V. K. Ivanov, and L. V. Chernysheva, Phys. Lett. 59A, 191 (1979).

[2]G. Wendin, in *Photoionization and Other Probes of Many-Electron Interactions*, edited by F. J. Wuilleumier (Plenum, New York, 1976), p. 61.

[3]A. W. Fliflet, R. L. Chase, and H. P. Kelly, J. Phys. B 7, 1443 (1974).

[4]A. Zangwill and Paul Soven, Phys. Rev. Lett. 45, 204 (1980).

[5]F. Combet Farnoux, in *Proceedings of the International Conference on Inner Shell Ionization and Future Applications, Atlanta, Georgia, 1972*, edited by R. W. Fink *et al.* (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1973), Vol. 2, p. 1130.

[6]R. Rabe, K. Radler, and H. W. Wolff, in *VUV Radiation Physics*, edited by E. E. Koch *et al.* (Vieweg-Pergamon, Berlin, 1974), p. 247.

[7]J. P. Connerade and M. W. D. Mansfield, Proc. Roy. Soc. London Ser. A 341, 267 (1974).

[8]F. C. Brown, R. Z. Bachrach, and N. Lien, Nucl. Instrum. Methods 152, 72 (1978).

[9]H. J. Hagemann, W. Gudat, and C. Kunz, J. Opt. Soc. Am. 65, 742 (1975).

[10]P. W. Palmberg, J. Vac. Sci. Technol. 12, 379 (1975).

[11]P. R. Woodruff, L. Torop, and J. B. West, J. Electron. Spectrosc. Relat. Phenom. 12, 133 (1977).

[12]M. P. Seah and W. A. Dench. Surf. Interface Anal. 1, 2 (1979).

[13]C. S. Fadley, Prog. Solid State Chem. 11, 265 (1976).

[14]J. P. Connerade, Contemp. Phys. 19, 415 (1976).

[15]T. C. Chiang, D. E. Eastman, F. J. Himpsel, G. Kaindl, and M. Aono, Phys. Rev. Lett. 45, 1846 (1980).

[16]G. Wendin and A. F. Starace, J. Phys. B 11, 4119 (1978).

[17]U. Fano, Phys. Rev. 124, 1866 (1961).

[18]G. Wendin, in *VUV Radiation Physics*, edited by E. E. Koch *et al.* (Vieweg-Pergamon, Berlin, 1974), p. 225.

[19]J. B. West, P. R. Woodruff, K. Codling, and R. Houlgate, J. Phys. B 9, 407 (1976).

[20]M. Y. Adam, F. Wuilleumier, N. Sandner, S. Krummacher, V. Schmidt, and W. Melhorn, Jpn. J. Appl. Phys. 17, 170 (1978).

[21]M. Y. Adam, F. Wuilleumier, N. Sandner, V. Schmidt, and G. Wendin, J. Phys. (Paris) 39, 129 (1978).