Population of the Three Major Exit Channels in the 3*d* Resonance Region of Atomic Gallium

Manfred O. Krause
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

Franco Cerrina
Synchrotron Radiation Center, University of Wisconsin–Madison, Stoughton, Wisconsin 53589

and

Anders Fahlman[a]
Department of Physics and Measurement Technology, Linköping Institute of Technology, S-58183 Linköping, Sweden

(Received 10 February 1983)

The exit channels in the region of the $3d \rightarrow 4p$ resonance of atomic gallium were determined in a photoemission experiment. The population of the three major channels involving $4p$ and $4s$ electrons was measured by the constant-ionic-state method for twenty resonant states between 18.8 and 21.7 eV, and the angular distribution of the emitted electrons was obtained. As a result, an autoionization case in which many resonances and many continua are coupled has been characterized in the most comprehensive experiment to date.

PACS numbers: 32.80.Dz, 32.80.Fb

We report here on the comprehensive characterization of a complex resonance, the $3d \rightarrow 4p$ resonance of atomic gallium, by identification of the exit channels and determination of their population and angular distribution parameter. Thus our work will provide important criteria to be met by theoretical calculations yet to be made for this autoionization case of many resonances coupled to many continuum exit channels. In addition, since the exit channels involve outer electrons, $4s$ and $4p$, the study of atomic gallium will aid in the interpretation of resonance effects in chemical and solid-state systems, where for example the resonance in GaAs had previously been associated with bulk or surface core excitons.[1]

In this experiment, electron spectrometry was combined with synchrotron radiation to study the exit channels continuously in the region of the numerous $3d \rightarrow 4p$ resonance states recently seen by Connerade[2] in photoabsorption. Except for a study[3] of the simpler cases of Kr and Xe, other related work, for example, on Ba[4] and Mn,[5] was limited in scope. A He I spectrum of Ga was reported by Dyke *et al.*[6]

We used our previously described apparatus[7] at the Wisconsin Synchrotron Radiation Source. Gallium was evaporated from a Ta oven at 1100 K and a background pressure around 5×10^{-6} Pa. A Seya monochromator with a 1440-lines/mm Os-coated grating provided a photon beam with a polarization of $p \approx 0.96$ and a bandpass of 1.6 Å as measured in an auxiliary photoelectron spectrometry for the analysis of x rays[8] experiment. Photoelectron spectra (PES) were recorded at the angles 0°, 55°, and 90° for several photon energies. A typical PES result is presented in Fig. 1, showing the relative intensities of the three exit channels associated with the resonance state at 20.33 eV. In the dipole approximation, these in-

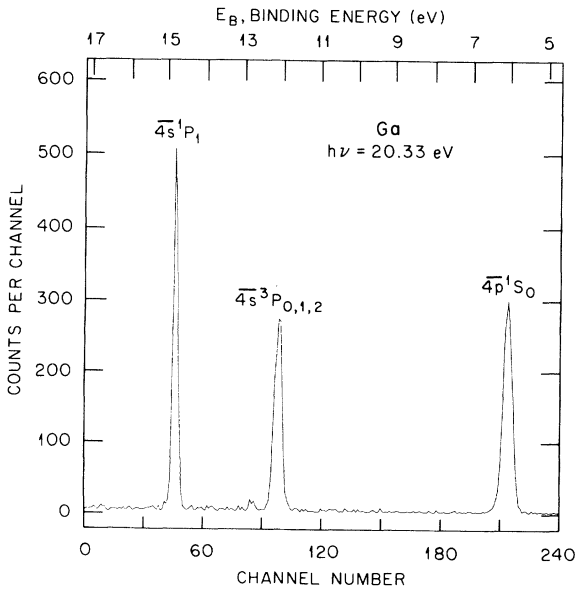

FIG. 1. Photoelectron spectrum of atomic gallium as recorded. Bandpass 1.6 Å, $\Delta E/E = 0.010$, $\varphi = 55°$.

tensities, I_i, are related to the partial widths or cross sections, Γ_i, of the channel i by[8]

$$I_i \propto \Gamma_i[1+\tfrac{1}{4}\beta_i(1+3p\cos 2\varphi)], \quad (1)$$

where p is the polarization of the photon beam and φ the observation angle relative to $p_\parallel$. We note that the relation (1) becomes independent of the angular distribution parameter β for a given pair of p and φ values. In this experiment, $p=0.96$ and $\varphi=55°$.

The relative partial width of each of the channels, $\overline{4p}\,^1S$, $\overline{4s}\,^3P$, and $\overline{4s}\,^1P$,[9] was measured by setting one analyzer to $\varphi=55°$ and synchronously advancing the photon energy and the electron acceleration energy in equal steps, but opposite directions, to pass, at any photon energy, the electron of a given channel through the analyzer. This lock-in procedure, which we call the constant-ionic-state (CIS) method, was an essential feature of the experiment. It appears that this is the first use of the CIS method in the study of free atoms, although it has been used in one molecular[10] any many solid-state studies.[11,12] According to Eq. (1), the parameter β_i can be determined from measurements at two angles φ. Again as for Γ_i, the CIS method was employed, this time using two analyzers simultaneously, one in the 0° and the other in the 90° position. All CIS data were stored in a multiplexed multichannel analyzer, while system control and data analysis were done by computer.

In Fig. 2, the CIS-Γ and CIS-β spectra are shown for the $\overline{4p}\,^1S$ channel over the full extent of the $3d \rightarrow 4p$ resonance. Each spectrum, composed of 160 25-meV steps, required 1 h recording time. Spectra were corrected for background, 1 to 2 counts compared with about 1000 counts at 20.33 eV (peak 14). The CIS-Γ spectra were normalized to the photon flux and the grating efficiency which was obtained from CIS-Γ spectra of Xe $5p_{3/2}$ and Ar $3p$ reference levels.[8] The labeling of Fig. 2 corresponds to that of Ref. 2. The CIS-Γ spectra for the $\overline{4s}\,^3P$ and $\overline{4s}\,^1P$ channels are incorporated in a summary figure, Fig. 3, in which the relative partial widths are normalized at $h\nu=20.33$ eV (peak 14) to the relative intensities obtained from the PES spectrum of Fig. 1. The top spectrum in Fig. 3 represents the sum of the individual spectra.

This sum spectrum bears great resemblance to the absorption spectrum.[2] This is not surprising since radiative widths should be negligible and widths of two-electron channels were found to be small in extended-range PES spectra, namely

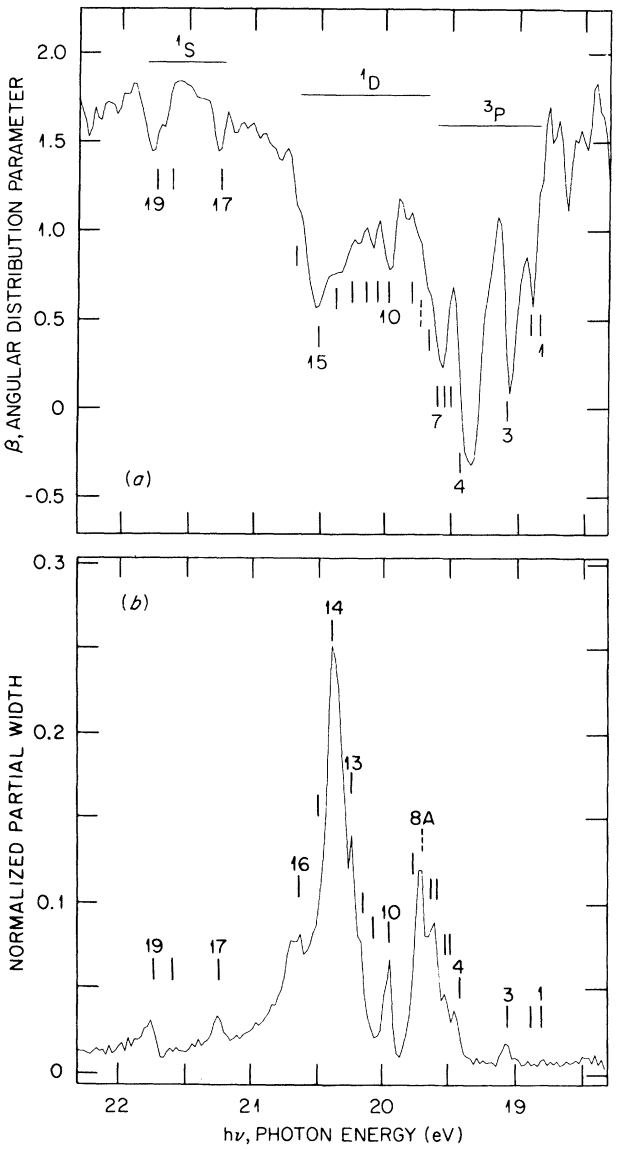

FIG. 2. (a) β parameter and (b) relative cross section or width for the $\overline{4p}\,^1S$, ϵl exit channel, measured continuously in the CIS mode of operation across the resonance with use of a photon bandpass of about 45 meV. Labels are those of Ref. 2.

about 5% of the total at $h\nu=20.33$ eV. Hence the number of important exit channels is three[13] in terms of the $^{2S+1}L,\epsilon l$ notation, and the resonance processes are well described by the scheme of Fig. 4. The $4p$ and $4s$ electrons are ejected by direct photoionization and by resonance ionization. At resonance energies strong enhancement occurs amounting to 100 times the interpolated "background" cross section at $h\nu=20.33$ eV. As seen from Fig. 3 and from Table I, which displays the numerical results of a graphic peak fit-

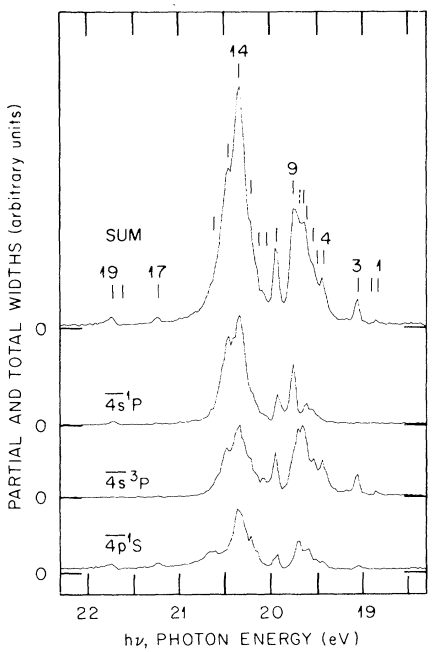

FIG. 3. Partial widths of exit channels and total width of $3d \rightarrow 4p$ resonance of Ga. Estimated errors are 5% for normalization of the CIS-Γ spectra with the aid of the PES spectrum of Fig. 1, and 15% for skewing from end to end of each spectrum.

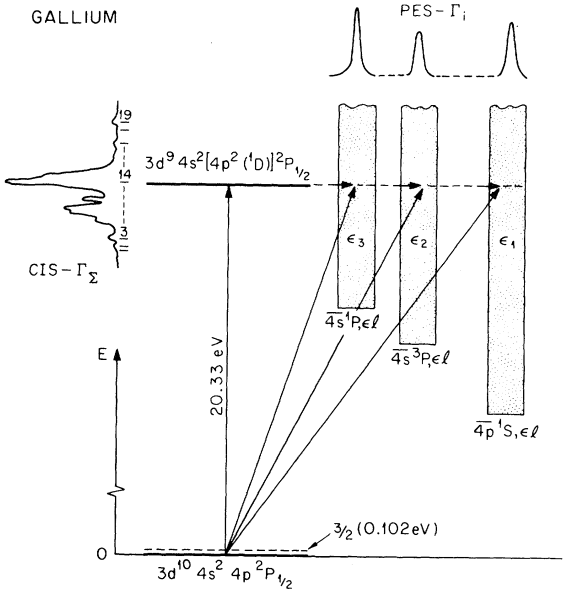

FIG. 4. Schematic representation of the photoionization processes in the $3d \rightarrow 4p$ resonance region of gallium.

ting of the CIS-Γ spectra, all three channels are usually populated. While the $3d^9 4s^2(4p^2\,{}^1D)^2S$, ^2P, ^2D states couple with all channels showing a slight preference for $\overline{4s}\,^3P,\epsilon l$, the $3d^9 4s^2(4p^2\,{}^3P)^2D$ and, to some extent, the $3d^9 4s^2(4p^2\,{}^3P)^2P$ states couple strongly with $\overline{4s}\,^3P,\epsilon l$, and the $3d^9 4s^2(4p^2\,{}^1S)^2D$ states couple strongly with $\overline{4p}\,^1S,\epsilon l$. This suggests that the coupling between the $4p^2$ manifold and the final ionic state of the same symmetry is more important than the coupling to the $3d$ hole and the continuum electron.

Interference between direct and resonance transitions manifests itself in the "classical" Fano-Beutler profiles[14] of peaks 16 to 19; see Fig. 2(b). However, "normal" peak shapes without pronounced tails and dips are best suited to describe the remaining structure. The absence of interference shapes can be attributed to an overwhelming strength of the resonance channel and/or the coupling of many closely spaced strong resonances with common continua, which according to the autoionization theory by Mies[15] will lead to such normal peaks.

When resonances occur the variation of the β parameter is an important corollary to the change in Γ. As Fig. 2 shows, enhancement of Γ at a resonance state is accompanied by a dip in the β value. The dip is most pronounced for the $4p^2\,{}^3P$ resonance states and relatively shallow for $4p^2\,{}^1S$. Although we have no CIS-β spectra for the other two exit channels, PES data obtained at fifteen photon energies indicate a similar behavior with a tendency toward generally lower β values.

At the temperature of 1100 K used in this experiment the population of the $^2P_{3/2}$ state of gallium is 0.41, while at $T \approx 1700$ K used in the absorption experiment[2] the population is 0.50. As a consequence, the resonance states originating from the thermally occupied ground state $^2P_{3/2}$ are more intense in the spectrum of Ref. 3 than in our spectrum (Fig. 3). This thermal effect, which is especially noticeable for the peaks 1, 13, and 15, confirms the assignments of many states.

In summary, this study yielded the highly differentiated data needed for the description of a complex autoionization resonance. These data can provide a sensitive test for theoretical calculations and should be useful for interpreting resonance effects in gallium compounds and solids.

We are grateful to J. W. Taylor for the use of the Os grating, to J. A. Weaver for lending his computer, and to the Synchrotron Radiation Cen-

TABLE I. Population of (i) resonance states (column 3) and (ii) exit channels (columns 4 to 6) by photoionization of gallium between 18.8 and 21.7 eV. Each population is normalized to 100%.

Peak No. (a)	Resonance State (a)	Sum (b)	$\overline{4p}\,^1S$	$\overline{4s}\,^3P$	$\overline{4s}\,^1P$
1	$^*(^3P)^2D$	0.2	20	80	--
2	$(^3P)^2D$	0.5	10	90	--
3	$^*(^3P)^2D$	2.3	12	81	7
3A	(c)	1.8	4	68	28
4	$^*(^3P)^2P$	4.0	12	77	11
5	$^*(^3P)^2P$	4.6	14	64	22
6	$(^3P)^2P$				
7	$(^3P)^2P$	9.1	18	57	25
8	$^*(^1D)^2S$				
8A	---	7.3	32	62	6
9	$(^1D)^2S$	6.3	≤ 5	≤ 8	≥ 87
10	$^*(^1D)^2P$	7.5	16	51	33
11	$(^1D)^2P$	2.1	12	68	20
12	$^*(^1D)^2D$	3.7	37	44	19
13	$^*(^1D)^2P$	7.8	33	39	28
14	$(^1D)^2P$	20.2	25 (d)	30 (d)	45 (d)
15	$^*(^1D)^2D$	13.7	18	27	55
16	$(^1D)^2D$	5.7	37	27	36
17	$^*(^1S)^2D$	1.3	69	15	16
18	$^*(^1S)^2D$	0.3	75	25	--
19	$(^1S)^2D$	1.6	62	7	31
All Peaks		100.0	23 (e) ±1	40.5 (e) ±1.5	36.5 (e) ±1.5

[a] Notations of Ref. 3; asterisk indicates transitions from thermal $^2P_{3/2}$ ground state. Our energy values agree with those of Ref. 2 within 20 meV.

[b] From the analysis of top spectrum of Fig. 3.

[c] Structure from 19.1 to 19.3 eV.

[d] Reference values from PES spectra at 20.33 eV.

[e] Integrated from the respective CIS spectra before partitioning.

ter staff for their dependable operation of the photon source. This work was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corporation; the Synchrotron Radiation Center is supported by National Science Foundation Grant No. 8020164.

[a] On sabbatical leave at the Oak Ridge National Laboratory.

[1] G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).

[2] J. P. Connerade, Proc. Roy. Soc. London, Ser. A 354, 511 (1977).

[3] D. L. Ederer, A. C. Parr, J. B. West, D. Holland, and J. L. Dehmer, Phys. Rev. A 25, 2006 (1982).

[4] R. A. Rosenberg, M. G. White, G. Thornton, and D. A. Shirley, Phys. Rev. Lett. 43, 1384 (1979).

[5] R. Bruhn, E. Schmidt, H. Schröder, and B. Sonntag, Phys. Lett. 90A, 41 (1982).

[6] J. M. Dyke, G. D. Josland, R. A. Lewis, and A. Morris, Mol. Phys. 41, 967 (1981).

[7] M. O. Krause, T. A. Carlson, and P. R. Woodruff, Phys. Rev. A 24, 1374 (1981).

[8] M. O. Krause, in *Synchrotron Radiation Research*, edited by H. Winick and S. Doniach (Plenum, New York, 1980), pp. 101–157.

[9] We use the hole designation: e.g., $\overline{4p}\,^1S \equiv 4s^2\,^1S$ (ground state $4s^2 4p\,^2P$).

[10] E. W. Plummer, T. Gustafsson, W. Gudat, and D. E. Eastman, Phys. Rev. A 15, 2339 (1977).

[11] G. J. Lapeyre, J. Anderson, P. L. Gobby, and J. A. Knapp, Phys. Rev. Lett. 33, 1290 (1974).

[12] F. Gerken, J. Barth, and C. Kunz, in *X-Ray and Atomic Inner-Shell Physics—1982*, edited by B. Crasemann, AIP Conference Proceedings No. 94 (American Institute of Physics, New York, 1982), pp. 602–614.

[13] This applies also to the two-electron excitation states reported in Ref. 2.

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

[15] F. H. Mies, Phys. Rev. 175, 164 (1968).