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MEASUREMENT OF THE ELECTRON ENERGY SPECTRUM RESULTING FROM A DOUBLE AUGER PROCESS IN ARGON*

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We previously[1] found that in the readjustment to a K vacancy in neon, 7.5% of the Auger transitions involved the ejection of two electrons. Similar results were obtained as the consequence of forming a hole in the L shell of argon[2] or M shell of krypton,[3] in which double Auger processes occurred, respectively, $9 \pm 1\%$ and $31 \pm 4\%$ of the time. In each of these processes the electrons were both ejected from the outermost valence shell. One possible source for this extra ionization can come from a sudden change in effective charge that leads to electron shake-off.[4] With the use of Hartree-Fock single-electron wave functions, the shake-off probabilities for the above-mentioned double Auger processes were calculated to be about 0.5%, which was, however, more than an order of magnitude lower than the observed values. The earlier investigations[1-3] on the double Auger process were based on measurements of the relative abundances of the differently charged ions that result from the readjustment to an inner-shell vacancy. A measurement of the energy distribution of the electrons ejected in the double Auger process should be of great value in evaluating the phenomenon. In this paper we present the results of such a study on the $L_{\mathrm{II,\,III}}MMM$ transition in argon.

Our experiment consists of irradiating argon with x rays in an electron spectrometer, and measuring the energy spectrum of electrons emitted in the readjustment to holes in the $L_{\mathrm{II,\,III}}$ shell. The spectrometer and experimental procedures have been previously described.[5] The x-ray source is a carbon target of a Henke design to prevent contamination from the tungsten filament. The tube is operated at 2 keV and the x rays are filtered through 250 $\mu g/cm^2$ of polystyrene. The principal source of x rays is the carbon K_α band. Contributions to the electron spectra that could arise from bremsstrahlung have been estimated from separate experiments to be negligible. The x rays from the C K_α band, which has an average energy of 278 eV with a "half-width" of 8 eV, possess enough energy to eject electrons from the L_{II} and L_{III} but not the L_{I} shell of Ar. Satellite Auger lines that might have occurred from transition in Ar^{2+} have been virtually eliminated by the use of the C K_α band, since the energies of the x rays are generally not capable of ejecting electrons simultaneously from the L and M shells.[6] Experiments were carried out in the gas phase and efforts were made to insure that the electrons observed came only from the single and double Auger processes. For example, electrons en route from the source volume to the analyzer are susceptible to inelastic collision with neutral atoms, as the result of which they appear at lower energies. This effect has been corrected for by means of measuring the spectrum as a function of pressure and extrapolating the results to zero pressure. Aside from the above-mentioned effect,

the background came essentially from only the noise of the detector system. This background was constant over the spectrum and its value was four counts per channel per day.

In Fig. 1 we have plotted the spectrum of electrons from 80 to 225 eV. These data have been corrected for counter background, pressure effects, variation with energy of the width of the energy window, and the efficiency of electron detection. Error bars have been inserted for several points throughout the spectrum to indicate uncertainties derived from counting statistics. The hatched area is the contribution due to the double Auger process.

In Table I we have compared results from this experiment with theory. The energies for the Auger lines, E, are given in electron volts and are based on the value[7] of 206 ± 2 eV assigned to the $2p\,3p\,3p$ transition. The energies are also given as ΔE, the difference in energy from the $2p\,3p\,3p$ transition. The energy assigned to the continuum spectrum is for its threshold. The theoretical values for ΔE have been obtained from spectroscopic tables[8] and may be regarded as having a high precision. The theoretical values for E have been obtained from the differences in total energies for the initial and final states of the Auger process as obtained from Hartree-Fock wave functions[9] with configuration mixing for the appropriate singly and doubly charged ions. These wave functions were also used in computing electron shake-off probabilities by a method described earlier.[10] The results of the calculations include transitions to excited but bound states as well as to the continuum. The shake-off calculations are then weighted by the relative Auger rates,[11] and those transitions leading to the same final state are summed to obtain the relative probabilities for the different double Auger process-

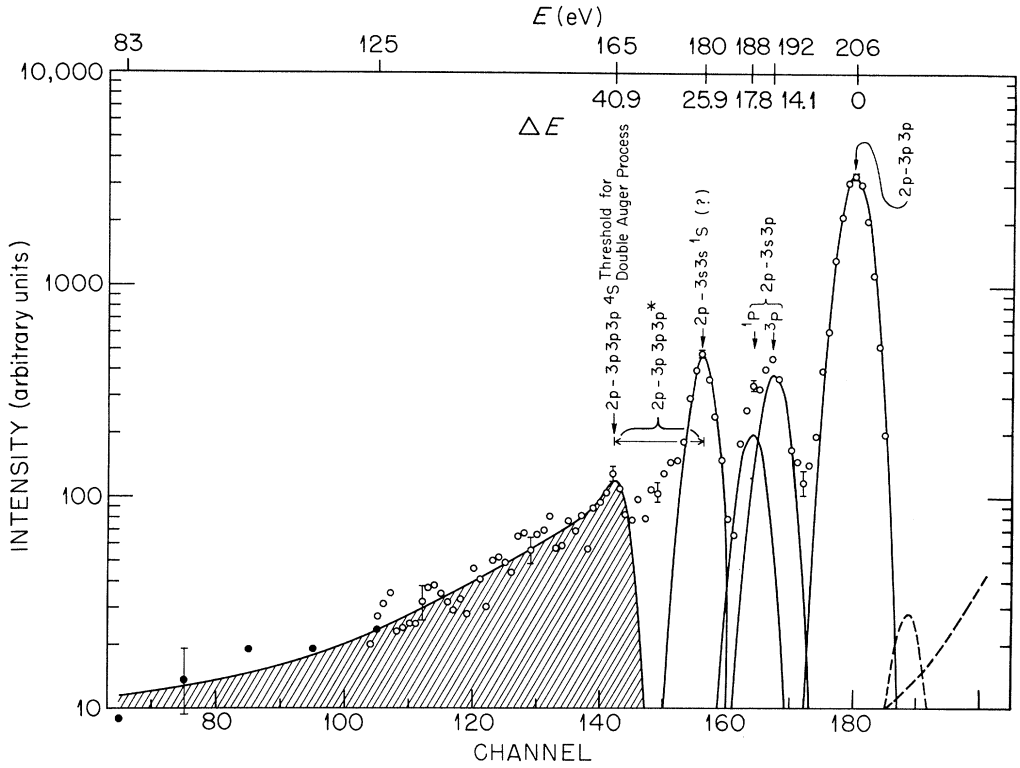

FIG. 1. Plot of the electron spectrum, fully corrected for background, that is the result of Auger processes filling the L_{II} and L_{III} holes formed by C $K\alpha$ x rays. Error bars are plotted arbitrarily throughout the spectrum to indicate uncertainties due to counting statistics. The dots, circles, and dashed line are data from three runs at different ranges. The hatched area represents the contribution to the double Auger process. The higher energy end of the spectrum given by the dashed line includes contributions of double electron ejection arising from photoionization in the M shell of argon, which will be reported separately. This contribution has a negligible effect on the charge spectrum. Between 180 and 165 eV there may be a series of lines corresponding to the transition $2p$-$3p\,3p\,3p^*$ where two of the $3p$ electrons are removed from the atom, while a third is placed into a higher orbital.

Table I. Comparison of experiment and theory for the L Auger spectrum in Ar.[a]

	Experimental						Theory		
	Energy[b] (eV)				Relative transition probability		Energy (eV)		Relative transition probability
Transition	ΔE CK[c]	ΔE M[d]	E CK	E M	CK	M	ΔE[e]	E[f]	
$2p\,3p\,3p\,{}^3P$		0		206.5		0.4	0	207.8	0.41[g]
$2p\,3p\,3p\,{}^1D$	(0)	1.9	(206)	204.6	(1.00)	0.5 } 1.0	1.7	205.7	0.50[g] } 1.00
$2p\,3p\,3p\,{}^1S$		3.9		202.6		0.1	4.1	202.7	0.09[g]
$2p\,3s\,3p\,{}^3P$	14.2	14.1	192	192.4	0.12	0.1	14.1	190.7	0.17[g]
$2p\,3s\,3p\,{}^1P$	17.4	17.8	189	189.1	0.06	0.05	17.8	183.0	0.17[g]
$2p\,3p\,3p\,3p^*, 4p\,{}^3P$	(26.2)	26.1	(180)	180.4	0.13	0.05	25.9	...	...
$2p\,3s\,3s\,{}^1S$		27.2		179.3		0.06	...	167.5	0.02[g]
$2p\,3p\,3p\,3p$	40.7	...	165	...		...	40.9	...	0.0043[h]
$2p\,3p\,3p\,3s$	...	...	...	...	(0.16)	...	...	...	0.0037[h] } 0.0087
$2p\,3p\,3s\,3s$	...	...	...	...		...	...	...	0.0007[h]
Ratio of double to single Auger processes			0.12 ± 0.04[c] 0.10 ± 0.01[i]						0.006[h]

[a]The average values for unresolved peaks are enclosed by parentheses.

[b]Energy of the Auger lines or threshold of the continuum spectra.

[c]This paper.

[d]W. Mehlhorn, preliminary unpublished results, to be published. A mean value is given for doublet lines arising from the splitting between the L_{II}, L_{III} levels.

[e]Obtained from C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[f]Obtained from Hartree-Fock wave functions with configuration interaction.

[g]R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

[h]Calculated from electron shake-off probabilities using single-electron Hartree-Fock wave functions. These probabilities include transitions both to excited and to continuum states.

[i]T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. 10, 455 (1965).

es. The total probability for a double Auger process is insensitive to the weighting, since the calculated probabilities were approximately the same, regardless of the particular LMM Auger process.

In Table I are also listed some recent results of Mehlhorn,[12] who initiated inner L shell vacancies in Ar by electron bombardment. Because of the much higher intensities available from this method of excitation, he has been able to achieve extremely high resolution. His results on the discrete lines are in good agreement with ours. Of particular interest are two doublets that he finds corresponding to our unresolved peak at 180 eV. One doublet can be identified with an Auger process $2p$-$3p\,3p\,3p^*$ in which $3p^*$ stands for an electron initially in the $3p$ orbital that has been promoted into a higher shell, in this instance the $4p\,{}^3P$ state in Ar^{2+}. Mehlhorn has designated the other doublet as the $2p\,3s\,3s$ transition, but it is not inconceivable that it may be another transition of the type $2p$-$3p\,3p\,3p^*$, for example, one leading to the state $4p\,{}^1D$. Still other lines of less intensity may be expected for higher excited states up to the threshold for the double Auger process, as indeed seems to be the case (cf. Fig. 1).

The central interest of this paper lies in the continuum spectrum starting at the threshold for a $2p$-$3p\,3p\,3p$ double Auger process. This spectrum is a measure of one of the electrons involved in the double-electron ejection (the one with the higher energy). The spectrum for the other electron can be obtained from the relationship

$$E_T = E_1 + E_2, \tag{1}$$

where E_T is the total energy available for the double Auger process, that is, the difference in energy between Ar^+ (with a hole in the $2p$ shell) and Ar^{3+}. For the $3p^4\,{}^3P$ state this amounts to 165 eV and the spectrum will be distributed

symmetrically about 82.5 eV. E_1 and E_2 are the energies for electrons one and two. Since the observed spectrum for electron one is at its highest intensity at the threshold and drops continuously down to the half-way mark, the spectrum of electron two will have its highest value at zero energy and then drop monotonically with increasing energy. The total intensity for a double Auger process (the hatched area in Fig. 1) relative to the rest of the Auger spectrum is in agreement with the earlier measurement using charge spectrometry (cf. Table I). The error in the present experiment includes uncertainties of the various corrections to the spectrum as well as counting statistics.

The description given above of the electron spectrum for a double Auger process is qualitatively that of a shake-off process in which a high-velocity electron (in this case an Auger electron) gives up a small portion of its energy to a low-energy shake-off electron. Similar spectra have been obtained[13] in the photoionization of inner shells. In these studies both the spectral shape and total probability for electron shake-off gave excellent agreement with calculations based on single-electron wave functions. Although the double Auger process involving two electrons ejected from the outermost shell has the qualitative appearance of electron shake-off, the calculated probabilities (see Table I) based on single-electron wave functions are more than an order of magnitude lower than experiment. Why? We feel that the answer to this question probably resides in the fact that the two electrons are removed from the same shell, where one can no longer accurately describe the nature of multiple ionization without including correlation between the electrons. (A similar conclusion[14] has been reached in the case of double electron ejection as the result of photoionization of the outermost shell.) The problem requires a many-body solution. That is, the transition probability for a double Auger process is proportional to the square of the dipole matrix element

$$M_d = \int \psi_f(r_1, r_2, r_3)\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right) \times \psi_i(r_1, r_2, r_3) d\tau_1 d\tau_2 d\tau_3, \quad (2)$$

where ψ_i and ψ_f, which include electron correlation, are the initial and final wave functions for the three electrons involved in the transition. It can be easily shown[14] that a solution based on Eq. (2) will include both dipole and monopole contributions. A many-body approach to the problem of a double Auger process is being currently worked on by Russek.[15]

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[1]T. A. Carlson and M. O. Krause, Phys. Rev. Letters 14, 390 (1965).

[2]T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. 10, 455 (1965).

[3]M. O. Krause and T. A. Carlson, Phys. Rev. 149, 52 (1966).

[4]For example, electron-shake off arising from Auger process has previously been treated by M. Wolfsberg and M. L. Perlman, Phys. Rev. 99, 1833 (1955); T. A. Carlson and M. O. Krause, Phys. Rev. 137, A1655 (1965).

[5]M. O. Krause, Phys. Rev. 140, A1845 (1965). See also M. O. Krause, Phys. Letters 19, 14 (1965).

[6]Mehlhorn has found the energy necessary to eject electrons simultaneously from the $2p$ and $3p$ shells of argon to be 280.0 to 285.5 eV (private communication).

[7]As obtained in a separate experiment by comparing the Auger peak with a photopeak that represents ionization of the $3p$ shell in argon; T. A. Carlson, to be published. Mehlhorn has recently re-examined this transition with high resolution, and finds a four-line spectrum having a weighted average of 204.9 eV. W. Mehlhorn, to be published.

[8]C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[9]Calculated from a code of C. Froese.

[10]The probability for shake-off is given by

$$P = 1-[|\int \psi_f^*(nlj)\psi_i(nlj)dr|^2]^N - NP_F,$$

where ψ_i and ψ_f are the initial and final single-electron wave functions for a given shell nlj, N is the number of electrons in nlj, and P_F = is a correction from transition to filled states. See T. A. Carlson and M. O. Krause, Phys. Rev. 140, A1057 (1965). N.B.: Eq. (8) of this reference has a misprint: 1 should stand outside the brackets. The calculations reported, however, were carried out with the correct formula.

[11]R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

[12]W. Mehlhorn, preliminary unpublished results, to

be published.
[13]M. O. Krause, T. A. Carlson, and R. K. Dismukes, to be published. See also Bull. Am. Phys. Soc. 11, 353 (1966).
[14]T. A. Carlson, to be published. See also Ref. 2.
[15]A. Russek, private communication.

COEXISTENCE CURVE OF He^4 NEAR THE CRITICAL POINT

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The coexistence curve of He^4 has been measured over the range 0.1 mdeg $< T_c - T <$ 250 mdeg. The data for $T_c - T < 100$ mdeg fit an expression of the form $|\rho - \rho_c| \propto (P_c - P)^{\beta_P} P$, where ρ is the density of either the liquid or the vapor, and P is the pressure; $\rho_c = 0.0701 \pm 0.0006$ g/cm^3, $P_c = 1705.0 \pm 0.8$ Torr [$T_c = 5.1890 \pm 0.0006$°K], and $\beta_P = 0.355 \pm 0.004$.

The nature of the gas-liquid critical point has interested both experimentalists and theoreticians for many years. Recent data indicating significant deviations from the classical molecular-field theory for a number of substances have prompted interest in more careful experiments on a wide variety of systems and in different ways to describe the phenomena theoretically. The model of a two-dimensional lattice gas[1] finds direct application to critical phenomena and predicts for the coexistence curve a relation of the form $|\rho - \rho_c| \propto (T_c - T)^{\beta_T}$, where ρ is the density of either the liquid or the vapor, and the exponent, β_T, has been determined to be very close to $\frac{5}{16}$ for this model.[2] The molecular-field theory of Landau and Lifshitz,[3] when applied to the critical point, predicts $\beta_T = \frac{1}{2}$; several extensions and modifications of this theory[4-7] also predict $\beta_T = \frac{1}{2}$ for data close enough to the critical point. Other expressions proposed for the coexistence curve include that of Fisher,[8] who suggests $(\rho_L - \rho_G) \propto t^{\beta_1}(t+\alpha)^{\beta_0 - \beta_1}$, where t is $(T_c - T)/T_c$ and α is a function of the quantum parameter Λ^*.[9] If $\beta_1 = \frac{1}{2}$ and $\beta_0 = \frac{1}{3}$, then this function behaves like t^β with $\beta = \frac{1}{3}$ for $t \gg \alpha$ and $\beta = \frac{1}{2}$ for $t \ll \alpha$. Also, Edwards[10] has suggested that his He^4 data are fitted by a function proposed by Buckingham[11] of the form $T_c - T \propto X^2/(1 - \ln X)$, where X is $(\rho_L - \rho_G)/(\rho_L + \rho_G)$. [Over the range of our data, this expression is essentially equivalent to $X \propto (T_c - T)^\beta$ with $\beta = 0.41$.] Recently, Sherman[12] has measured the coexistence curve of He^3 and reported that $\beta_T = 0.34$ for $(T_c - T)/T_c$ between 3×10^{-1} and 3×10^{-2} but changes to 0.48 ± 0.02 for $(T_c - T)/T_c$ less than 2×10^{-2}. This paper presents accurate data on He^4 near its critical point; we find that the coexistence curve can be fitted by the expression $|\rho - \rho_c| = A(T_c - T)^{\beta_T}$ with $\beta_T = 0.352 \pm 0.003$ and $A = 0.054$ over a range for $(T_c - T)/T_c$ between 2×10^{-5} and 2×10^{-2}, and where the T_{58} temperature scale[13] has been used to convert vapor pressures into temperatures.

In order to avoid any flat topping of the coexistence curve due to the gravity effects[14-16] that arise when only the average density of tall samples of fluid are measured near the critical point, we have chosen a capacitive technique of density measurement. The sample helium is admitted between two closely-spaced, horizontal capacitor plates (see Fig. 1), and the dielectric constant of the helium is measured. Assuming that the molar polarizability, α, of the fluid helium is strictly constant, then the density, ρ, of the helium is obtained from the dielectric constant, ϵ, by the Clau-

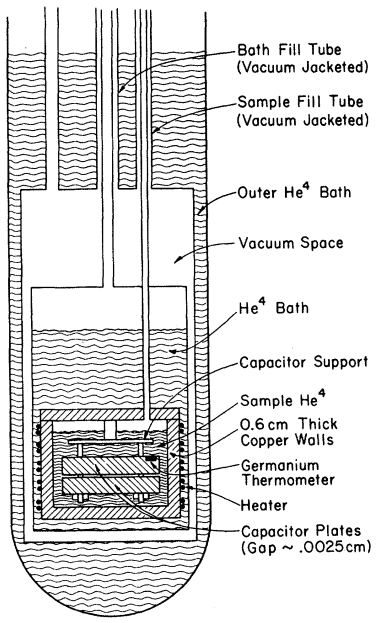

FIG. 1. Schematic drawing of apparatus.