High-Resolution $L_{2,3}M_{4,5}M_{4,5}$ Auger Spectrum of Free Zinc Atoms

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The high-resolution $L_{2,3}M_{4,5}M_{4,5}$ Auger-electron spectrum from zinc vapor has been measured using electron-impact excitation. The spectrum has been decomposed into components and interpreted by comparison with calculated line energies and intensities. The calculations have been carried out for *jj* coupling in the initial states and for intermediate coupling with configuration interaction in the final states. Good agreement between the calculated and the experimental results has been found.

The $L_{2,3}M_{4,5}M_{4,5}$ spectrum of solid zinc has recently been studied by several authors.[1-5] The present measurements of zinc vapor were undertaken in order to facilitate the interpretation of the results of these studies. For the same purpose we also calculated the line energies and intensities for the atomic $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum of zinc. For a reliable interpretation of the separate line components of the measured line groups the calculated line intensities are needed in addition to the energies. Zinc has a closed-subshell electron ground-state configuration $(\ldots 3s^23p^63d^{10}4s^2)$ and is purely monoatomic in the vapor phase, which simplifies the theoretical calculations. From the experimental point of view the vapor pressure of zinc is high, which means that fairly low oven temperatures are needed to give a sufficient particle density of zinc atoms in the target region.

The experimental spectra after background subtraction and instrumental-dispersion correction are shown in Figs. 1 and 2. The final experimental points are averages from several consecutive runs. The apparatus used will be described in detail elsewhere,[6] therefore only the most important experimental conditions will be given here. The measurements were carried out by means of an energy analyzer of the cylindrical-mirror type. The energy resolution $\Delta E/E$ of the spectrometer was 0.05%. The primary electron beam was typically 200 μA at 2.5 keV and the zinc vapor pressure was approximately 5×10^{-4} Torr in

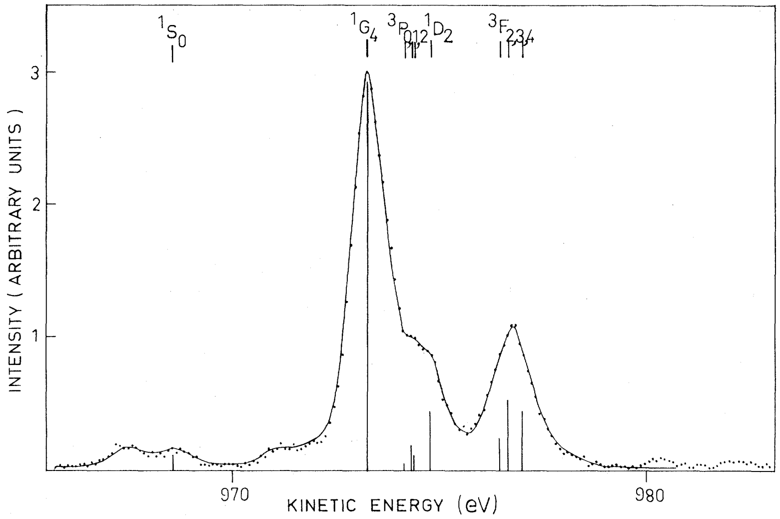

FIG. 1. The separation of the experimental $L_3M_{4,5}M_{4,5}$ spectrum into its different components. The experimental results are described by the points and the sum of the components by the solid line.

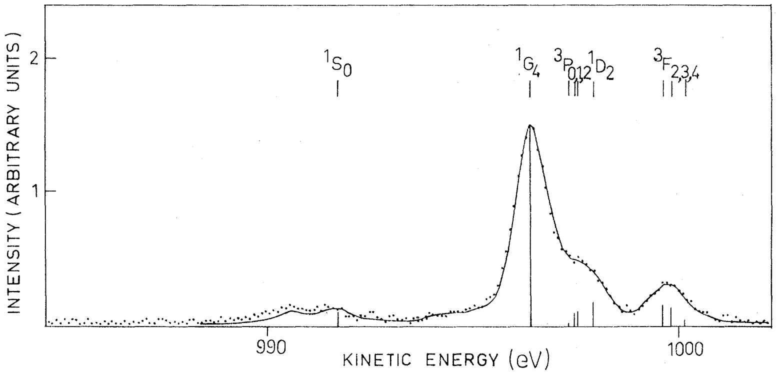

FIG. 2. The separation of the $L_2M_{4,5}M_{4,5}$ spectrum into its components.

the target region of the oven. The mean emission angle of the analyzed Auger electrons with respect to the direction of the primary beam was 54.5°, corresponding to the first-order focusing mode of the cylindrical-mirror analyzer. With this specific value of the emission angle, the effects of the angular distribution of the Auger electrons can also be neglected.

The separation of the different components of the line groups was accomplished by a computer program using as the standard line shape the line obtained from the highest peak of the $L_3M_{4,5}M_{4,5}$ group. Thus 1.0 eV was obtained for the full width at half-maximum of the standard line. The same standard linewidth was used for both groups. The contribution of the spectrometer broadening to this width was 0.5 eV, which was nearly the same as the natural width of the Auger lines. The effects of inelastic scattering on the observed spectrum were tested by measuring the spectrum of the primary electrons scattered from the target region with the same energy as that of the Auger electrons. The spectrum is shown in Fig. 3. The elastic-peak width 0.09% also contains the portion of the thermionic energy distribution of the electrons emitted by the tungsten filament. The inelastically scattered electrons form a peak separated by 5.8 eV from the main peak of elastically scattered electrons. This effect was taken into account by using a standard curve consisting of two peaks separated by 5.8 eV, and having the intensity ratio of elastically to inelastically scattered primary electrons with this kinetic energy. The double-peak structure on the low-energy side of the line groups can be identified as a combination of the inelastic peak associated with the $^1G_4$ component and of the ordinary $^1S_0$ component. In these regions there is also an inelastic background from $^3P_{0,1,2}$ and $^1D_2$ lines.

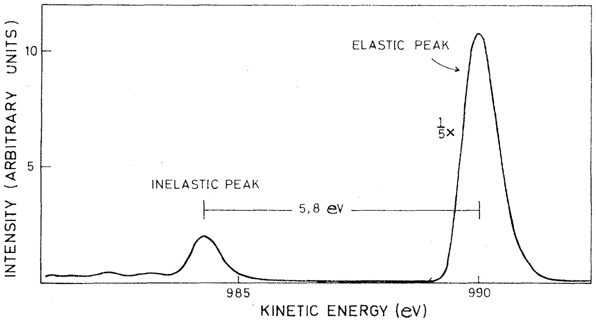

FIG. 3. The energy loss spectrum of the primary electrons scattered from zinc vapor.

The energy values used for positioning of the line groups were taken from our recent work,[7] in which the calibration was based on the known energies of argon and neon Auger lines. As pointed out previously[7] the line energies differ considerably from the values obtained from solid zinc.

Our calculations of the relative energies and intensities of the lines have been made in the customary two-hole representation. In the initial state the inner-shell hole is coupled to a hole in the continuum representing the missing Auger electron, and in the final state the two vacancies are coupled. The double-vacancy final-state configuration ($3d^{-2}$) of the $L_{2,3}M_{4,5}M_{4,5}$ Auger transition gives rise in the intermediate coupling scheme to the levels $^1S_0$, $^1D_2$, $^1G_4$, $^3P_{0,1,2}$, and $^3F_{2,3,4}$. The spin-orbit interaction and the configuration interaction between the final-state configurations $3s^{-2}$, $3s^{-1}3d^{-1}$, $3d^{-2}$, $4s^{-2}$, $3s^{-1}4s^{-1}$, and $3d^{-1}4s^{-1}$ have been taken into account. The calculation procedure is the same as that used recently for the Auger spectra of cadmium[8] and xenon.[9] For the numerical values of the radial integrals $D(\lambda, 1')$ and $E(\lambda, 1')$, the values given by

TABLE I. Theoretical and experimental relative energies (in eV) of the $L_{2,3}M_{4,5}M_{4,5}$ Auger diagram lines of zinc. Column *a*: *LS* coupling. Column *b*: intermediate coupling without configuration interaction. Column *c*: intermediate coupling with configuration interaction. The experimental errors are given in parentheses.

	Theory (*a*)	Theory (*b*)	Theory (*c*)	Experiment
$^3F_4$	4.17	4.18	4.18	3.75 (0.10)
$^3F_3$	3.88	3.88	3.88	3.41 (0.10)
$^3F_2$	3.65	3.68	3.69	3.22 (0.10)
$^1D_2$	1.42	1.49	1.89	1.51 (0.15)
$^3P_2$	0.98	0.90	1.17	1.12 (0.20)
$^3P_1$	0.84	0.84	1.09	1.07 (0.20)
$^3P_0$	0.76	0.78	1.04	0.93 (0.20)
$^1G_4$	0	0	0	0 (0.05)
$^1S_0$	−5.81	−5.83	−4.52	−4.68 (0.15)

McGuire[10] were used. The calculated and the experimental line energies of the final-state levels relative to the $^1G_4$ level are given in Table I and the relative intensities in Table II. For comparison, the theoretical values are given in *LS* coupling, and in intermediate coupling with and without configuration interaction. The spin-orbit diagonal matrix element have been included in the *LS* coupling scheme.

A comparison between the experimental and the theoretical line energies shows that the energy splitting in the spectrum is in general smaller than that obtained from theory. The line intensities calculated in the intermediate-coupling scheme with and without configuration interaction agree well with the experimental results. The fact that the effect of the configuration interaction on the theoretical results is rather small indicates that electron correlation plays only a minor role in the $L_{2,3}M_{4,5}M_{4,5}$ spectrum of zinc.

For the intensity ratio of the $L_2M_{4,5}M_{4,5}$ and $L_3M_{4,5}M_{4,5}$ groups, the value $1:(2.3 \pm 0.15)$ has been obtained, which agrees fairly well with the value $1:2.13$ calculated from the number of electrons in the L_2 and L_3 subshells and corrected by the slightly different ionization cross sections from the formula of Gryzinski.[11] The observed natural width of the Auger lines, 0.5 ± 0.15 eV,

TABLE II. Theoretical and experimental relative intensities (in percent) of the $L_{2,3}M_{4,5}M_{4,5}$ Auger diagram lines of zinc. The experimental errors are given in parentheses. Column *a*: *LS* coupling. Column *b*: intermediate coupling without configuration interaction. Column *c*: intermediate coupling with configuration interaction in the final states.

Transition		Theory						Experiment	
		a)		b)		c)			
$L_2M_{4,5}M_{4,5}$	$^3F_4$	7.2		5.8		5.8		1.7	
	$^3F_3$	8.1	22.4	8.1	19.4	8.0	19.0	5.4	13.6 (1,0)
	$^3F_2$	7.1		5.5		5.2		6.5	
	$^1D_2$	10.3		9.6		10.3		7.3	(1.0)
	$^3P_2$	0.6		2.9		2.5		3.8	
	$^3P_1$	1.0	2.0	1.0	4.3	1.3	4.2	3.5	7.5 (2.0)
	$^3P_0$	0.4		0.4		0.4		0.2	
	$^1G_4$	63.6		64.9		64.1		67.6	(1.0)
	$^1S_0$	1.7		1.8		2.4		4.0	(1.0)
$L_3M_{4,5}M_{4,5}$	$^3F_4$	10.8		11.6		11.4		8.7	
	$^3F_3$	7.2	22.4	7.1	23.3	7.1	23.1	10.5	23.7 (1.0)
	$^3F_2$	4.4		4.6		4.6		4.5	
	$^1D_2$	10.3		9.2		9.6		8.8	(1.0)
	$^3P_2$	1.4		2.4		2.3		1.8	
	$^3P_1$	0.5	2.0	0.5	3.1	0.6	3.1	3.2	5.4 (2.0)
	$^3P_0$	0.1		0.2		0.2		0.4	
	$^1G_4$	63.6		62.8		62.0		60.1	(1.0)
	$^1S_0$	1.7		1.6		2.1		2.0	(1.0)

is somewhat smaller than the theoretical value 0.76 eV, obtained from the transition probabilities of McGuire.[12] According to our observations the widths of the Auger lines are very nearly the same for both groups, in contradistinction to the photoelectron measurements by Yin *et al.*[3] from solid target. This may mean that the $L_2L_3M_5$ Coster-Kronig transition is possible in the metal because of the effect of extra-atomic relaxation,[1] but this transition is cut off in free atoms, in which relaxation energy is not available. According to Table II of Yin *et al.*,[3] where the widths of L_2 and L_3 vacancy states are computed from Green's potential, the result is that the L_2 width is reduced from 0.865 eV in the solid to 0.63 eV in the free atom, which is nearly the same as the 0.65 eV L_3 width.

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Molecular Ordering and Even-Odd Effect in a Homologous Series of Nematic Liquid Crystals[*]

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Order parameters have been measured in a homologous series of nematic liquid crystals, *p*-alkoxyazoxybenzenes, by ^{13}C NMR. The ordering exhibits an even-odd alternation along the series, and a comparison of our data at the isotropic-nematic transition temperatures is made for the first time with a recent theory of Marčelja which explicitly accounts for end-chain interactions between the molecules. Some conclusions are drawn concerning molecular conformational motion and ^{14}N spin relaxation in the nematic phase.

Although molecular end chains are known to have perceptible and important effects on the properties of liquid crystals, theories of the liquid crystal phase have not until recently, included their effects explicitly. Rather, their influence was taken into account indirectly by assuming simply that they "take up space" and thus affect the average interaction between essentially rigid molecules.[1] Marčelja has now presented a theory which accounts specifically for the effects of the end chains on the anisotropic interactions between the molecules.[2] This theory provides good agreement with experimental data on isotropic-nematic transition temperatures and entropies, and explains for the first time the "even-odd" effect in these quantities along a homologous series.[3] A quantity of prime concern in the structure of the nematic phase is the degree of orientational molecular ordering, described by an order parameter[4]:

$$S = \langle P_2(\cos\theta) \rangle , \tag{1}$$

where θ is the angle between the long molecular axis and the nematic director. A striking prediction of the theory is that S should depend significantly on the end chains and should also exhibit the even-odd effect in a homologous series. In this Letter we present the results of measurements of the core order parameter for a homologous series of nematic liquid crystals at the isotropic-nematic transitions and lower in the nematic phase. These data provide the first convincing