High-resolution L x-ray spectrum of In

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The L x-ray spectrum of indium has been measured in fluorescence by using a double-crystal spectrometer. The relative energies, relative intensities, and the natural widths of the diagram lines are determined and compared to the theoretical calculations as well as x-ray photoemission spectroscopy data. The results show that the energies of transitions involving L_1, $M_{2,3}$, and N_1 shells are shifted 3—9 eV from the theoretical self-consistent-field energies. There also exists a discrepancy in the theoretical and experimental linewidths of these transitions. The cause of these effects is discussed.

I. INTRODUCTION

As Krause[1] and Chen *et al.*[2] have pointed out in their interpretations of L spectra of Zr and Ag,[3] there exist discrepancies between the theoretical and experimental lifetimes of $2s$ states. We have noticed the same discrepancy in our measurements on ^{41}Nb to ^{49}In.[4–6] There is very little exact experimental information about L spectra. The only high-resolution measurements of total L spectra, in this Z area, are the above mentioned, except for some measurements of our own group.[7–10]

We have published some data on L spectra of the elements ^{41}Nb to ^{51}Sb in our earlier papers,[5,6,10] and now we present the whole L spectrum of In, paying attention particularly to the relative intensities of the L lines and to their widths and relative energies.

After the papers of Krause[1] and Chen *et al.*,[2] new experimental[11,12] and theoretical[13–16] information about M and N shells has been published. The availability of x-ray photoemission spectroscopy (XPS) data on M and N shells gives us better possibilities to analyze more accurately the experimental widths of L shells obtained from x-ray spectra. The purpose of this work has been to measure with high resolution all L x-ray lines of In in order to obtain information about the transition energies of L lines and lifetimes of states.

II. EXPERIMENTAL

The L x-ray spectrum of In was measured by using a double-crystal spectrometer similar to that described by Suoninen and Pessa.[17] A Mo x-ray fluorescence tube operated at 40 kV×40 mA was used to induce L emission. The spectrometer was equipped with a pair of calcite crystals cleaved along the (211) axis ($2d$=0.606 nm).

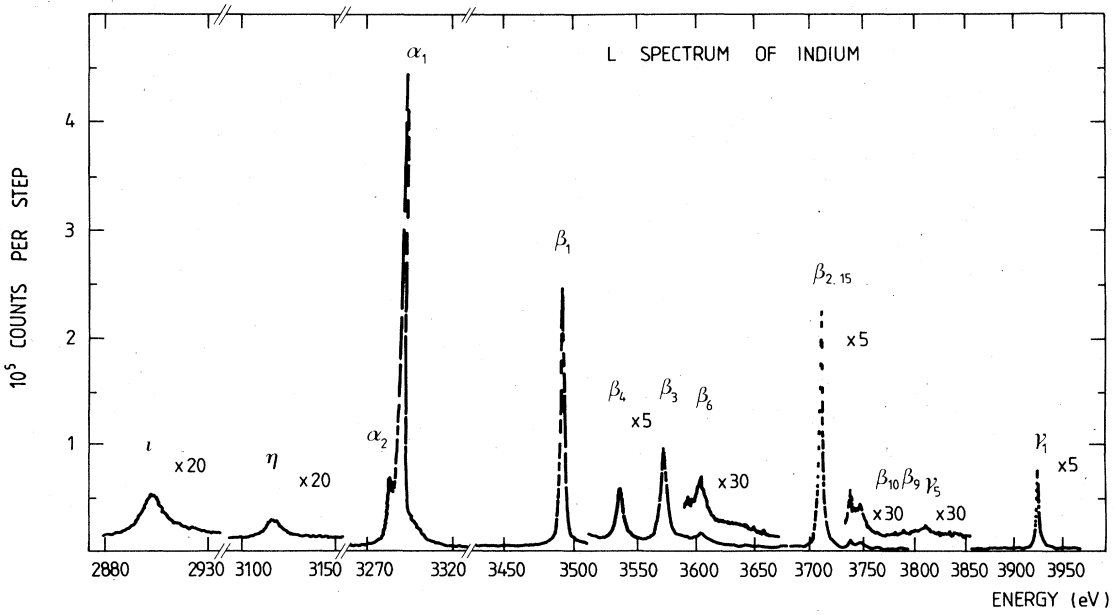

FIG. 1. Measured L x-ray spectrum of In. No corrections have been made.

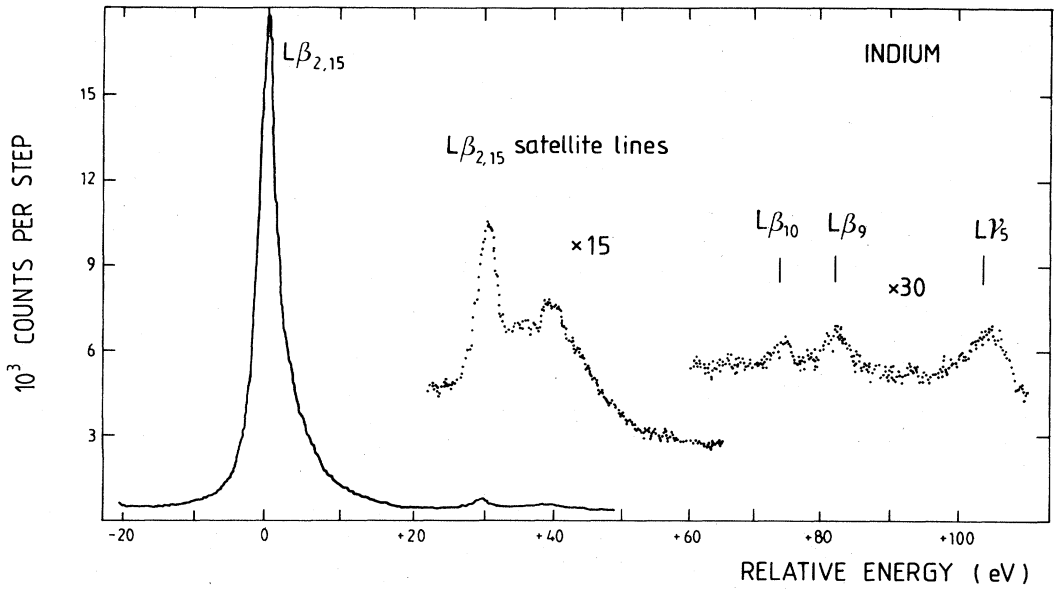

FIG. 2. Enlarged part of the L x-ray spectrum of In which shows the $L\beta_{2,15}$-satellite structure.

The rocking-curve full width at half maximum (FWHM) for the In $L\beta_1$ line was 0.35 eV in the $(1,-1)$ position. This indicates that the spectrometer resolution is sufficiently good to obtain detailed information about the linewidths. A piece of spectroscopically pure In sheet was used as a sample.

The spectrum was recorded stepwise by changing the Bragg angle θ of the second crystal in steps of 17 seconds of arc, and several successive single spectra were summed up. A single measurement can cover an energy range which corresponds to about one degree in angle θ.

To determine the natural linewidths, the measured spectrum was corrected for the background radiation and the crystal response. No corrections for the influence of the collimator, self-absorption of the target and absorption of the crystals were made.

III. RESULTS AND DISCUSSION

A. Spectra

The measured L x-ray spectrum of In is illustrated in Fig. 1. The Ll and $L\eta$ lines are rather wide (10—12 eV), which is due to strong Coster-Kronig transitions to the M_1 shell. The $L\alpha$ spectrum is discussed in detail in a previous paper.[8]

The greatest discrepancy between theory and measurements is in the $L\beta_3$ and $L\beta_4$ lines whose intensities and linewidths are not as large as theoretically predicted. We shall discuss this point more extensively.

The $L\beta_{2,15}$ satellite spectrum is presented in more detail in Fig. 2. We can see the same main structures in the

TABLE I. Energies of the peaks of the L lines of In. The energy of the Ca $K\alpha$ line determined by Bearden is used as a standard to which all the other lines are referred (in eV).

Transition	Line	Reference line	Separation from the reference line	Error limit	E_{expt} this work	E_{expt} Ref. 19	E_{theory} Ref. 20	E_{theory} a
L_1M_2	$L\beta_4$	$L\beta_3$	38.2	0.4	3534.4	3535.3	3538.75	3535.75
L_1M_3	$L\beta_3$	$L\beta_6$	35.0	0.6	3572.5	3573.1	3577.28	3574.28
L_2M_4	$L\beta_1$	$L\beta_4$	48.4	0.2	3485.9	3487.2	3487.2	
L_2N_1	$L\gamma_5$	$L\beta_2$	102.8	0.6	3817.1	3815.9	3807.83	3817.33
L_3N_1	$L\beta_6$	Ca $K\alpha_1$	84.2	0.6	3607.5	3608.23	3599.95	3609.45
L_3N_4	$L\beta_2$	Ca $K\alpha_1$	22.6	0.4	3714.3	3713.8	3714.48	
L_1M_4	$L\beta_{10}$	$L\beta_2$	73.1	0.8	3787.4	3876.8	3793.64	3787.64
L_1M_5	$L\beta_9$	$L\beta_2$	80.6	0.8	3794.9	3794.2	3801.21	3795.21

[a]Theoretical values using corrections in Table II.

TABLE II. Theoretical binding energies E_B of in (eV).

Level	E_B[a]	Correction	E_B corrected
L_1	4252.10	−6[b]	4246.10
L_2	3946.29		
L_3	3738.41		
M_1	837.58		
M_2	713.35	−3[c,d]	710.35
M_3	674.82	−3[c,d]	671.82
M_4	458.46		
M_5	450.89		
N_1	138.46	−9.5[e]	128.96
N_2	96.43		
N_3	89.64		
N_4	23.93		
N_5	22.99		

[a]Reference 20.
[b]Reference 21.
[c]Reference 23.
[d]Reference 24.
[e]Reference 22.

satellites of In as observed by Parratt[3] in a study of Ag. The intensity of the satellites is about 5% of the intensity of the $L\beta_{2,15}$ diagram line. Chen *et al.*[2] have calculated from a Hartree-Fock-Slater potential model that an extra hole in the M shell shifts the $L\beta_2$ diagram line of Ag by 30—35 eV. Krause[1] has calculated the same shifts for Zr using a relativistic Hartree-Slater potential model. The shifts were about 27—28 eV for an extra M_3 or M_5 hole in Zr. Thus we may conclude that the satellite structure on the high-energy side of In $L\beta_{2,15}$ is due to extra holes in the M shell, which give rise to a shift of 30—40 eV. The satellite spectrum is very complicated; there are several tens of possibilities for satellites with an extra hole in the M shell. Chen *et al.*[2] and Tulkki *et al.*[18] have analyzed the $L\alpha$ satellite spectrum and concluded that it contains 30—40 lines. The situation in the $L\beta_{2,15}$ spectrum appears to be equally complicated.

The $L\beta_{10}$ and $L\beta_9$ lines are very weak but still distinguishable. $L\gamma_5$ and $L\gamma_1$ of the γ lines were recorded but the $L\gamma_{2,3}$ could not be measured with the available crystals.

B. Energies

The double-crystal spectrometer used in the measurements is not capable of absolute energy measurements, but it is capable of accurately measuring small energy intervals. In the case of In, the energy of the $K\alpha_1$ line of Ca was used as a standard [3691.68 eV (Ref. 19)]. The energies were measured from the peak of the line profile. The measured and theoretical[20] energies of L x-ray diagram lines of In are presented in Table I.

The accuracy of weak lines and those far from the standard line is limited in our measurement. We note, however, that the energies measured by us agree within the error limits to those of Ref. 19.

When comparing the measured and theoretical[20] energy values we notice that the energies of $L\beta_1$ (L_2M_4) and $L\beta_2$ (L_3N_4) do agree quite well with the theoretical energies calculated for neutral free atoms. The energies of $L\beta_4$ (L_1M_2) and $L\beta_3$ (L_1M_3) lines differ by −4 to −5 eV, $L\gamma_5$ (L_2N_1) and $L\beta_6$ (L_3N_1) by +8 to +9 eV, and $L\beta_{10}$ (L_1M_4) and $L\beta_9$ (L_1M_5) by −6 to −7 eV from those calculated in Ref. 20. These calculations do not include the energy shift caused by nonradiative (Auger, Coster-Kronig) continua. According to Chen *et al.*[21] the interaction with the doubly-ionized Auger continua causes a shift in the L_1 binding energy of −3 to −6 eV in the Z area $30 \leq Z \leq 47$. The corresponding effect on the $L_{2,3}$ binding energy is small according to the calculations.

The effect of interaction with the Auger continua on M- and N-shell binding energies has been studied by Wendin and Ohno.[22—24] According to these calculations, the

TABLE III. Experimental and theoretical linewidths of L x-ray lines of In (in eV).

Transition line		Γ		Γ[b]	
		This work	Theory[a]	1	2
L_1M_2	$L\beta_4$	6.0	10.6	9.5	9.9
L_1M_3	$L\beta_3$	6.5	10.9	9.5	10.2
L_2M_1	$L\eta$	11.2	12.8	11.2	
L_2M_4	$L\beta_1$	3.0	3.0	2.9	2.8
L_2N_1	$L\gamma_5$	6.8	5.5	5.3(6.0)[c]	7.3
L_2N_4	$L\gamma_1$	2.7	2.6		
L_3M_1	Ll	11.1	12.6	11.0	
L_3M_4	$L\alpha_2$	2.83	2.8	2.7	2.7
L_3M_5	$L\alpha_1$	2.83	2.8		2.7
L_3N_1	$L\beta_6$	6.4	5.3	5.1(5.8)[c]	7.1
$L_3N_{4,5}$	$L\beta_{2,15}$	3.1	2.4		

[a]Theoretical L widths from Table V (column c) and M widths from Ref. 14 and N widths from Ref. 15 except N_1 from Ref. 16.
[b]Theoretical L widths (Table V, column c) and experimental M,N widths (N_1 width also from Ref. 16) from Table IV, Ref. 11 (case 1) and Ref. 12 (case 2).
[c]Reference 16.

TABLE IV. Theoretical and experimental M and N widths of In (in eV).

	Γ (theory) a	Γ (expt.) Ref. 11	Ref. 12	Γ (This work) (obtained from the line in parentheses)	
M_1	10.3[a]	8.7		8.7 ($L\eta$)	(8.8) (Ll)
M_2	3.7[a]	2.6	2.99		
M_3	4.0[a]	2.6	3.30		
M_4	0.5[a]	0.4	0.33	0.5 ($L\alpha_2$)	
M_5	0.4[a]		0.33	0.5 ($L\alpha_1$)	
N_1	3.0[b]	2.8(3.5)[b]	4.8	4.3 ($L\gamma_5$)	(4.1) ($L\beta_6$)
N_2					
N_3					
N_4	0.1[a]				
N_5					

[a]By interpolating from the values of Refs. 14 and 15 except N_1 from Ref. 16.
[b]Reference 16.

shift for $M_{2,3}$ shells for elements $Z>30$ is -3 eV, while the shift for the Xe N_1 shell is -9.5 eV. To approximate the effect of these calculated corrections to the transition energies of In we adopt a shift value of -6 eV to correct the binding energy of the L_1 level. The theoretical binding energies[20] and corrections to them are presented in Table II. If we adopt the value of -3 eV for the shift in the $M_{2,3}$ binding energy and -9.5 eV for the shift in the N_1 level, and calculate the theoretical transition energies for In shown in Table I, we notice that the measured and corrected theoretical energies agree with an accuracy of about 1 eV. Hence it seems that the theories of Chen *et al.* and Ohno and Wendin may be used to explain the discrepancies between the results of Ref. 20 and experiments.

Energy shifts in L x-ray emission spectra of the elements Nb to Sb are discussed in more detail in Ref. 5.

It has to be realized that calculations do not yet include solid-state effects which are very difficult to calculate. hence it may be possible that some discrepancy remains due in part to the solid-state effects which do not cancel in transition energies.

C. Linewidths

We expect that the x-ray emission spectrum is well described by the convolution of the spectral functions of the initial and final states, the corresponding spectral functions are Lorentzian profiles. Thus the observed linewidths are related to the natural widths of the initial and final states. The state width, on the other hand, depends on the radiative (R), Auger (A), and Coster-Kronig (C) transition rates. For example, for the $L\beta_3$ line we have

$$\Gamma(L\beta_3)=\Gamma(L_1)+\Gamma(M_3) \quad (1)$$

and the L linewidth can be calculated from the equation

$$\Gamma(L_i)=\hbar(R_i+A_i+C_i)\ . \quad (2)$$

Using the predictions of McGuire[25] for radiative transition rates and of Chen *et al.*[26] for the Auger and Coster-Kronig transition rates of the L shell, along with theoretical[15,16] and empirical[11,12] M- and N-level widths, we have computed the theoretical linewidths of the L lines of In

TABLE V. L level widths of In (in eV).

Level	Transition used	Experiment a	b	Theory c	Ref. 31
L_1	L_1M_2	3.4	3.0	6.92	5.00
	L_1M_3	3.9	3.2		
L_2	L_2M_4	2.6	2.7	2.49	2.72
	L_2N_1	4.0(3.3)[d]	2.0		
L_3	L_3M_4	2.4	2.5	2.33	2.65
	L_3N_1	3.6(2.9)[b]	1.6		

[a]$M(N)$ widths from Ref. 11 (16).
[b]$M(N)$ widths from Ref. 12.
[c]Obtained from Eq. (2) with theoretical transition rates from Refs. 25 and 26.
[d]Reference 16.

TABLE VI. Theoretical and experimental intensities of L x-ray diagram lines of In.

		Theory[a]				
		With full rates		L_1-$L_3M_{4,5}$ Rate divided		
Transition	Line	b	c	b	c	Expt.
L_1M_2	$L\beta_4$	13.3	9.0	5.8	4.0	4.4
L_1M_3	$L\beta_3$	21.9	14.9	9.6	6.5	7.8
L_1M_2	$L\gamma_2$	2.6	1.8	1.2	0.8	
L_1M_3	$L\gamma_3$	4.4	3.0	1.9	1.3	
L_2M_4	$L\beta_1$	51.8	51.4	52.3	51.8	53.5
L_2M_1	$L\eta$	1.5	1.5	1.5	1.5	1.2
L_2N_1	$L\gamma_5$	0.3	0.3	0.3	0.3	
L_2N_4	$L\gamma_1$	6.6	6.5	6.7	6.6	3.5
L_3M_1	Ll	4.2	4.2	4.2	4.2	3.0
L_3M_5	$L\alpha_1$	100	100	100	100	100
L_3M_4	$L\alpha_2$	11.3	11.3	11.3	11.3	8.2
$L_3M_{4,5}$	$L\beta_{2,15}$	14.2	14.2	14.2	14.2	11.3
L_3N_1	$L\beta_6$	0.8	0.8	0.8	0.8	0.3

[a]Calculated by the model of Krause (Ref. 1). Nonradiative rated from Ref. 26 and radiative rates from Ref. 30.

[b]$\mathcal{N}_{L_1}:\mathcal{N}_{L_2}:\mathcal{N}_{L_3}=1:1:2$.

[c]$\mathcal{N}_{L_1}:\mathcal{N}_{L_2}:\mathcal{N}_{L_3}=1:1,5:3$.

shown in Table III.

Agreement between our experimental and semiempirical linewidths seems to be good for L_2 and L_3 transitions. This indicates that either theoretical L_2 and L_3 Auger and Coster-Kronig transition rates are well predicted, or errors due to solid-state effects and other possible deficiencies in the theory cancel in the transition-rate calculation.

The situation is different for transitions from the L_1 level. Theoretical and experimental L widths are given in Table IV. As was pointed out in our previous paper, the theoretical L_1 transition rates are overestimated. According to the theory,[26] the L_1-$L_3M_{4,5}$ Coster-Kronig transitions amount to almost 60% of all the transitions to the L_1 level in indium. Radiative transition rates amount to less than 2% for the L_1 level. The L_1-$L_3M_{4,5}$ transitions are very sensitive to the energy of the outgoing electron. The calculations of theoretical Coster-Kronig transition rates[26] are based on theoretical L-shell Coster-Kronig energies.[27] These energies have been computed by the same method that has been employed previously for calculation of binding energies.[20] These theoretical binding energies do not agree with the experimental values,[19,22–24,28] even in free atoms, as discussed in Sec. III B.

It seems that the large calculated L_1 level widths are due to overestimated theoretical L_1-$L_3M_{4,5}$ transition rates based on Coster-Kronig energy calculations which do not include many-electron effects. In the case of Zr, Nb, and Ag, one gets better $L\beta_3$ linewidths if one divides the theoretical L_1-$L_3M_{4,5}$ Coster-Kronig transition rates by a factor of about 2.5. If we do the same for In, we get $\Gamma(L\beta_3)=7.8$ eV, while the measured value is 6.5 eV. Thus there is still a discrepancy between theory and experiment. We will examine this observation in more detail in a forthcoming study.

We are also able to examine M and N widths if we adopt the theoretical widths for L_2 and L_3 shells from Table V (case c). The theoretical[14] M_1 width calculated by McGuire seems to be about 1.5 eV too large. On the other hand, the theoretical M_1 width calculated by Ohno[29] (8.03 eV) is too small. Our experimental values (8.7 and 8.8 eV) agree well with those by Fuggle and Alvarado.[11]

Theoretical $M_{4,5}$ widths do agree with our measurements while there is again disagreement in the different measurements and theoretical values of the N_1 subshell width. The theory[16] gives $\Gamma(N_1)=3.03$ eV while our measurements give 4.3 eV (from $L\gamma_5$) and 4.1 eV (from $L\beta_6$) if we adopt the theoretical values from Table IV to $\Gamma(L_2)$ and $\Gamma(L_3)$. Previously, values of 2.8 eV by Fuggle and Alvarado[11] and 4.8 eV by Mårtensson and Nyholm[12] have been reported. The width of the N_4 subshell seems to be very small, as the theory[14] predicts.

D. Intensities

We have calculated the theoretical relative intensities of In diagram lines following the model of Krause[1] which has been previously used for Ag.[2] The theoretical and experimental intensities are listed in Table VI.

We have used two different approximations for the initial L-hole population $\mathcal{N}_{L_1}:\mathcal{N}_{L_2}:\mathcal{N}_{L_3}$. The first approximation (1:1:2) corresponds to the natural hole population, and the second (1:1,5:3), to the situation where L_1-$L_{23}M,N$ Coster-Kronig processes have changed the natural hole population of L levels. We have used the radiative transition rates of Ref. 30 and nonradiative rates of Ref. 26 and calculated the relative intensities first with full theoretical rates and then reduced the L_1-$L_3M_{4,5}$ rate by a factor of 2.5. We notice again that the theory overestimates L_1 transition rates. By dividing L_1-$L_3M_{4,5}$ transition rates by a factor of 2.5 we get better agreement between theory and experiment. This is in good agreement with the conclusion of our linewidth analysis.

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