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STATIC RELAXATION IN GERMANE AND THE ESTIMATION OF RELAXATION ENERGY DIFFERENCES FROM AUGER AND CORE BINDING ENERGIES OF GERMANIUM COMPOUNDS

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ABSTRACT

Auger and core electron spectra were measured for several germanium compounds in the gas phase. The $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra of GeH_4 were deconvoluted to determine the energies of the individual component peaks. The molecular relaxation energy of the GeH_4 M_{45} shell was taken to be the average difference between the experimental and calculated energies. Differences in the molecular relaxation energies of the other germanium compounds relative to GeH_4 were calculated using the chemical shifts of the ^1G components of the $L_3M_{45}M_{45}$ Auger spectra and of the Ge 3d core electrons.

1. Introduction

Recently Shirley[1-3] refined Asaad and Burhop's theory[4] for predicting the kinetic energies of Auger electrons by including additional relaxation effects. An Auger energy is given by the following expression

$$E(I,J,J) = E_B(I) - 2E_B(J) - \mathcal{F}(J,J) + R_J \qquad (1)$$

where the Auger process involves the core electron subshells I and J, E_B is the experimental binding energy of subshells I and J as given by X-ray photoelectron spectroscopy, $\mathcal{F}(J,J)$ represents the sum of the final-state coupling terms, and R_J corrects for static relaxation of the J subshell orbitals. The energies of KLL and LMM Auger processes are successfully predicted by this model[2,3].

We have measured the $L_3M_{45}M_{45}$ Auger spectra and the Ge 3d core electron spectra of several germanium compounds in the gas phase. In the case of GeH_4, the $L_2M_{45}M_{45}$ spectra were also measured, and both the $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra were decovoluted into their component peaks. The molecular relaxation energy for the M_{45} level in GeH_4 was taken to be the average difference between the experimental Auger energies and values calculated from Equation (1), neglecting molecular relaxation. Germane was selected for a thorough evaluation of Equation (1) because we believed that its relaxation energies would be approximately the same as those of a free atom of germanium, for which relaxation energies may be readily estimated.

Auger spectra of the other germanium compounds were not analyzed in detail because they closely resemble the GeH_4 spectra. However, differences in molecular relaxation energies of the M_{45} shell for these compounds were calculated from the ^1G $L_3M_{45}M_{45}$ Auger chemical shifts and the Ge 3d core electron chemical shifts using a simple extension of Equation (1). These relaxation energy differences, relative to GeH_4, were calculated without the use of approximate, estimated values.

2. Experimental

The spectra and chemical shifts reported in this paper were measured on the Berkeley iron-free, double-focussing magnetic X-ray photoelectron spectrometer[5]. Al K_α (1486.6 eV) radiation was used to obtain the Ge 3d chemical shifts and the GeH_4 Auger spectra. The remaining Auger energies were measured using Mg K_α (1253.6 eV) radiation. The samples were introduced into the spectrometer at a pressure of 30-50μ; argon gas was simultaneously introduced at a pressure of 20-30μ, and the Ar $2p_{3/2}$ line (248.45 eV) was used as the standard. The germanium compounds were prepared using standard methods and checked for purity by infrared spectroscopy and vapor pressure measurements.

3. Discussion of Results

The $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra for GeH_4 were deconvoluted and least-squares fitted to Lorentzian lineshapes. Each spectrum consists of five components corresponding to the possible J states of the final d^8 cation, namely ^1S, ^1G, ^3P, ^1D, and ^3F. These are illustrated in Figures 1 and 2. We have also measured the core binding energy of the M_{45} shell. Although we were unable to measure the energies of the L_2 and L_3 shells, these values may be accurately estimated using the M_{45} energy together with the energies of the germanium $L_{\alpha_{1,2}}$ and L_{β_1} X-rays. These correspond to L_3M_{45} and L_2M_{45} transitions, respectively. Because the energy difference between two atomic core levels is independent of chemical environment[6], the energy of an L level is simply the sum of the M_{45} energy and the energy of the appropriate X-ray. The final-state coupling term, $\mathfrak{F}(3d,3d)$, was evaluated using atomic, two-electron Slater integrals, and is given for each final state by the expression

$$\mathfrak{F}(3d,3d)_{i_A} = \alpha_{i_A}F_0(3d,3d) + \beta_{i_A}F_2(3d,3d) + \gamma_{i_A}F_4(3d,3d) \qquad (2)$$

The coefficients for each state appear in Reference 3. Theoretical energies for the $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra of GeH_4 were calculated using Equation 1, except that the static relaxation, $R_{M_{45}}$, was neglected. The experimental and calculated values, the differences between them, and the quantities used in calculating these energies are listed in Table I. The energy difference between experimental and calculated values for each state corresponds to the total static relaxation $R_{M_{45}}$. Because this term depends only on the final state, it should have essentially the same value for all the d^8 states. The differences between calculated and experimental values are reasonable constant, with an average value of 15.2 eV.

Table I

Energies and Related Quantities for the $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger Spectra of GeH_4

	STATE				
	^1S	^1G	^3P	^1D	^3F
$L_2M_{45}M_{45}$ exp.	1154.7(2)	1160.5(1)	1161.3(2)	1162.4(1)	1164.6(1)
$L_2M_{45}M_{45}$ calc.	1139.2	1145.4	1146.4	1146.9	1149.7
ΔE	15.5	15.1	14.9	15.5	14.9
$L_3M_{45}M_{45}$ exp.	1123.8(1)	1129.5(1)	1130.9(1)	1132.9(2)	1133.8(1)
$L_3M_{45}M_{45}$ calc.	1108.7	1114.9	1115.9	1116.4	1119.2
ΔE	15.1	14.6	15.0	16.5	14.6
$\mathcal{F}(3d,3d)^{\dagger}$	42.4	36.2	35.2	34.7	31.9
$E_B(3d)$			36.9(1)		
$E_{h\nu}\ (L_{\alpha_{1,2}})^{\dagger\dagger}$			1188.0		
$E_{h\nu}\ (L_{\beta_1})^{\dagger\dagger}$			1218.5		

All values in eV. Uncertainty in tenths for experimental values appears parenthetically.

†Values calculated using Slater integrals from Mann's Tables, Reference 9.

††X-Ray energies from Beardon's Table, Reference 15.

The static relaxation,* R_J, may be subdivided into three components: inner-shell, intra-shell, and outer-shell[3]. The outer-shell relaxation may be easily estimated[7] for a free atom using a polarization potential of Hedin and Johannson[8] together with the principle of equivalent cores [9]. Using Slater integrals from Mann's Tables[10], the M_{45} outer-shell relaxation for a germanium atom is calculated to be 5.6 eV for the valence electron configuration s^2p^2 and 5.7 eV for the configuration sp^3. For a molecule, the outer shells are the valence molecular orbitals, and thus, the outer-shell relaxation (which we shall refer to as the molecular relaxation) is not easily estimated.

The M_{45} relaxation energy has been calculated by Rosen and Lindgren [11] to be 10.6 eV for copper. The outer-shell relaxation for the single 4s electron is calculated, using the method previously outlined, to be 1.4 eV. Thus, the inner-shell plus intra-shell relaxation energy for the copper M_{45} level is 9.2 eV. Because the electronic configuration of a germanium core is the same as that of a copper core, the inner-shell plus intra-shell relaxation energies for the M_{45} levels should be nearly the same for both elements. We estimate the inner-shell plus intra-shell relaxation energy for the germanium M_{45} shell to be about 10 eV because the core levels of germanium have somewhat higher binding energies than those of copper, leading one to expect a greater relaxation energy for germanium than for copper.

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*The static relaxation energies calculated in References 7 and 11 are for photoelectric ionizations. As shown in Reference 1, the static relaxation energy for an Auger ionization is twice that for a photoelectric ionization.

The molecular relaxation energy for GeH_4 is the difference between the total static relaxation energy, 15.2 eV, and the estimated inner-shell plus intra-shell relaxation energy, 10 eV, or approximately 5.2 eV. This value, for a germanium atom in an sp^3 molecular environment, is close to the estimated free-atom value. This result is plausible because the $4a_1$ and $3t_2$ valence molecular orbitals of GeH_4 are closely related to the 4s and 4p valence atomic orbitals of germanium.

Differences in the M_{45} molecular relaxation energies of a series of compounds may be easily calculated from Equation 1 by making the approximation that core-electron chemical shifts do not depend upon the level measured[6]. We rewrite Equation 1 for energy differences:

$$\begin{aligned}\Delta E(L,J,J) &= \Delta E_B(L) - 2\Delta E_B(J) - \Delta R_J \\ &\simeq -\Delta E_B + \Delta R_J \qquad (3)\end{aligned}$$

The inner-shell and intra-shell relaxation for a difference should be zero, leaving only a difference in molecular relaxation energy. This is given by rearranging Equation 3:

$$\Delta R_J^{mol.} = \Delta E(L,J,J) + \Delta E_B \qquad (4)$$

Experimental values of the chemical shifts for the Ge 3d core level and the ^1G $L_3M_{45}M_{45}$ Auger line of some volatile germanium compounds are listed in Table II together with the corresponding $\Delta R_{M_{45}}^{mol}$ values. These energy differences do not depend upon our estimate of the inner-shell plus intra-shell relaxation energy for germanium. However, the approximate magnitude

Table II

Ge 3d Binding Energy, Ge $L_3M_{45}M_{45}$ Auger Chemical Shift, and the Difference in Molecular Relaxation Energies

Compound	ΔE_B (3d)	ΔE ($L_3M_{45}M_{45}$)	$\Delta R^{mol}_{M_{45}}$
GeH_4	0.0	0.0	0.0
GeH_3CH_3	-0.46	1.05	0.6
$Ge(CH_3)_4$	-1.27	3.14	1.9
GeF_4	4.65	-5.22	-0.6
GeH_3Cl	0.87	-0.10	0.8
$GeCl_4$	2.70	-0.49	2.2
GeH_3Br	0.75	0.31	1.1
$GeBr_4$	2.05	0.82	2.9

All values in eV. Uncertainty in experimental values ±0.05.

of the molecular relaxation energy, $R_{M_{45}}^{mol}$, for each compound may be obtained by adding 5.2 eV to each difference. A comparison of these energies with the atomic outer-shell relaxation energy shows that molecular relaxation energies may deviate by several electron volts from the free atom value. For GeF_4, the molecular relaxation energy is significantly lower than the atomic value despite the increased number of valence electrons. This result is undoubtedly a consequence of the high electronegativity and low polarizability of fluorine.

In calculating the differences in molecular relaxation, we have used GeH_4 as our reference compound for making comparisons. Because all of the compounds are covalent and tetrahedral one would expect that R_J^{mol} might be a simple function of the substituents. In accord with this expectation, the ratio $\Delta R_{M_{45}}^{mol}(GeX_4)/\Delta R_{M_{45}}^{mol}(GeH_3X)$ is approximately 3 for $X = CH_3$, Cl, and Br. It appears that $R_{M_{45}}^{mol}$, for a given substituent, is somewhat less than linearly proportional to the degree of substitution. Relaxation terms arise primarily from charge polarization during photoemission. Because R_J^{mol} measures a substituent effect, one should be able to correlate the relative polarizabilities of functional groups with ΔR_J^{mol}. One would expect a larger ΔR_J^{mol} to correspond to a greater polarizability. For the GeX_4 compounds, the ΔR_J^{mol} values suggest that the polarizability of the substituents increases in the order

$$F < H < CH_3 < Cl < Br.$$

This order is consistent with optically determined polarizabilities[12].

These relaxation energy differences can be helpful in explaining ESCA chemical shifts. The binding energy differences $E_B(HX) - E_B(X_2)$ for X = F, Cl, Br, are -2.7[13], -0.4[14], -0.1 eV[14], respectively. The small chemical shifts for chlorine and bromine compared to fluorine are difficult to explain on the basis of ground-state charge distributions. The $\Delta R^{mol}_{M_{45}}$ values in Table II, however, suggest that the molecular relaxation energy of X_2 is large compared to that of HX for X = Cl, Br and small for X = F. It is therefore reasonable that the observed HX, X_2 shifts for chlorine and bromine are much smaller than that for fluorine.

Acknowledgment

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Figure Captions

Fig. 1. GeH_4 $L_2M_{45}M_{45}$ Auger spectrum. The components listed in order of increasing kinetic energy are ^1S, ^1G, ^3P, ^1D, and ^3F.

Fig. 2. GeH_4 $L_3M_{45}M_{45}$ Auger spectrum. The components listed in order of increasing kinetic energy are ^1S, ^1G, ^3P, ^1D, and ^3F.

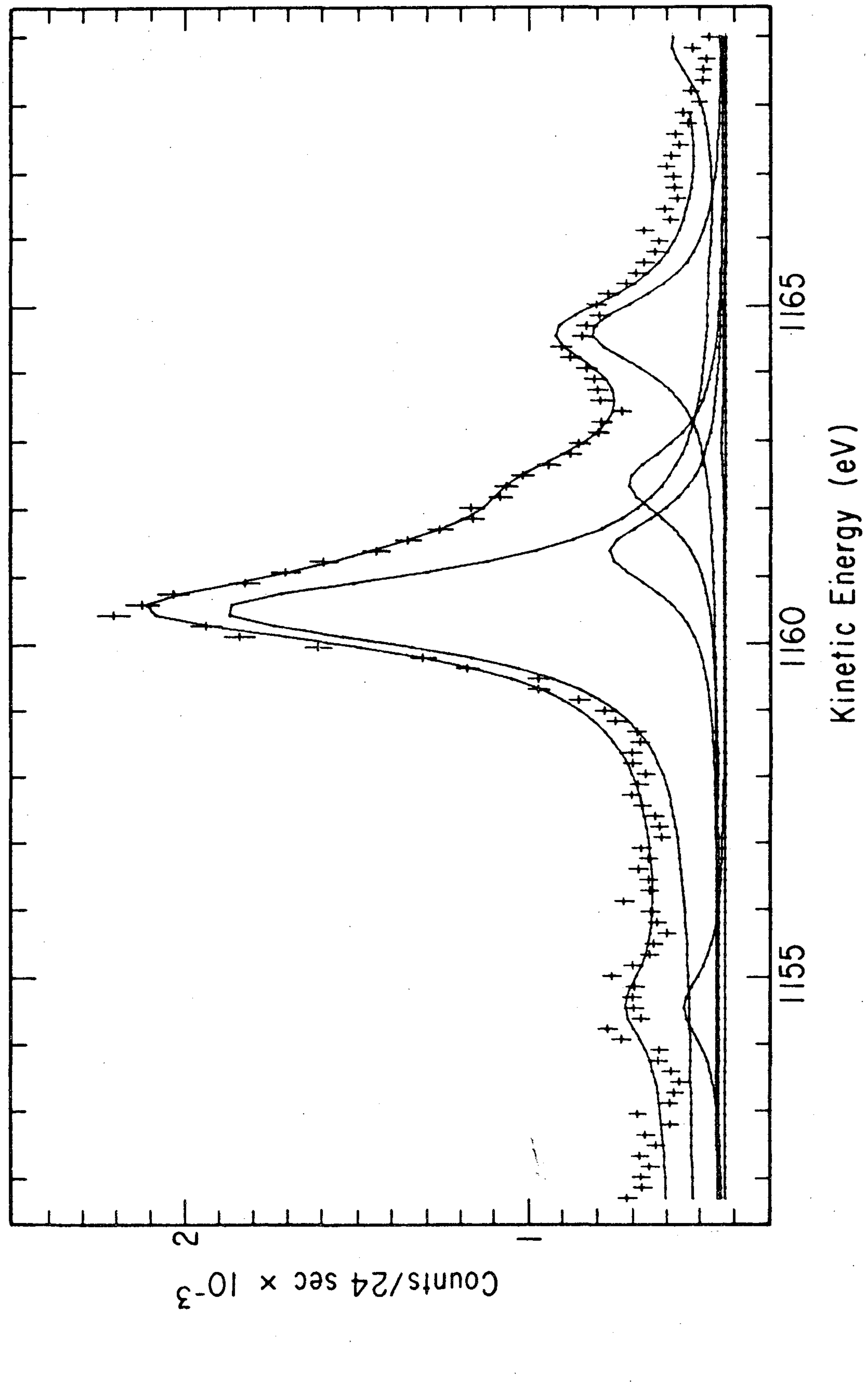

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Fig. 1

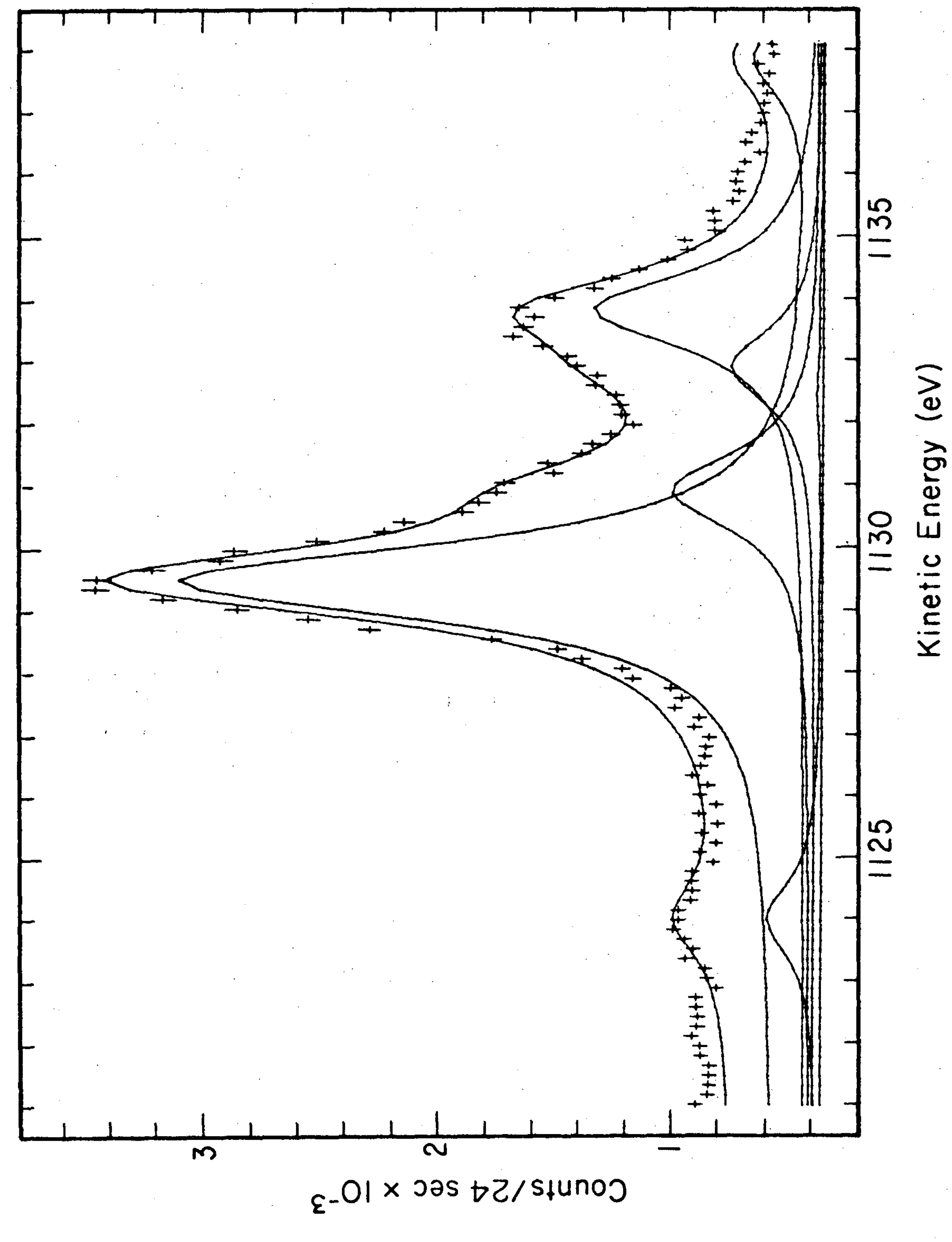

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Fig. 2