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Off-site interactions in the *CVV* Auger spectrum of noble metals: A study of silver

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The Cini-Sawatzky theory of *CVV* Auger transitions does not give simultaneous agreement with the position and line shape of the $M_{45}N_{45}N_{45}$ Auger spectrum of Ag. In accord with recent results for Au, this failure is attributed to the neglect of off-site interactions between the final-state holes. The magnitude of the discrepancy between theory and experiment for Ag is twice that found for Au and this is understood in terms of the difference in the ratio of off-site interaction to d-band width in the two metals.

I. INTRODUCTION

The concepts of electron screening and electron correlation are difficult to characterize accurately in metals. In a recent study of metallic Au,[1] it was shown that differences between the predictions of Cini-Sawatzky theory,[2–4] which includes only on-site interaction terms, and the experimental spectra of *CVV* Auger transitions, which create double-hole states in the d band, can yield information on the magnitude of off-site interactions and the screening between the holes. In this work we show that the discrepancy between Cini-Sawatzky theory and experiment for metallic Ag is twice as large as found for Au. This is related to differences in electron screening and correlation effects in the two metals, which we suggest arise from the different d-band widths of the two materials.

II. EXPERIMENT

Auger and photoelectron spectra of metallic Ag were measured using a high-performance Auger spectrometer described previously.[5] The specimen was cleaned by bombarding with 1-kV Ar^+ ions and the pressure in the analysis chamber was maintained at $\sim 10^{-10}$ mb during the experiment. Measurements of the O and C 1s photoemission lines showed the surface to be clean throughout the course of the experiment. Photoemission spectra were obtained using monochromated Al $K\alpha$ x rays and the Auger electron spectrum using Mg $K\alpha$ excitation. In all cases the analyzer was operated in fixed transmission mode at a resolution of 70 meV. Since the intrinsic linewidth of the $M_{45}N_{45}N_{45}$ Auger spectrum is of the order of 1 eV,[6] the experimental broadening of the spectrum is negligible. The photoemission spectra were collected with an instrumental resolution, determined by the monochromator, of 0.5 eV. The 3d lines were both found to have a lifetime broadening of 0.30 eV with binding energies of 374.3 and 368.3 eV for the $j=\frac{3}{2}$ and $\frac{5}{2}$ components, respectively.

The difference between these values and the measurements of the kinetic-energy scale of the Auger transitions was used to relate the Auger spectrum to the binding energy of the two-hole final states created by the transitions. The experimental $M_{45}N_{45}N_{45}$ Auger spectrum is shown in Fig. 1.

III. THEORETICAL DEVELOPMENT

The Cini and Sawatzky models[2–4] for *CVV* Auger transitions are based on Anderson and Hubbard Hamiltonians, respectively, retaining only intra-atomic Coulomb interactions U. Provided the valence-band density of states (DOS) is known, application of the Cini-Sawatzky theory involves essentially only one free parameter, namely the screened interaction U, which determines both the position and the line shape of the Auger

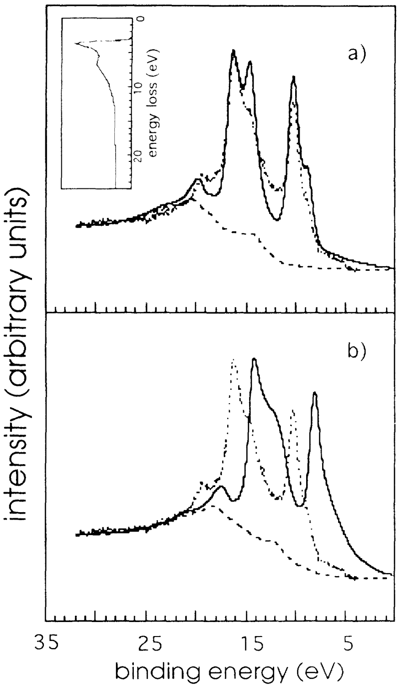

FIG. 1. Comparison between theoretical and experimental spectra for $M_{45}N_{45}N_{45}$ Auger transition in metallic silver. The zero binding energy corresponds to the Fermi energy for the M_5 group. In both (a) and (b), the theoretical spectrum is given by the solid curve, and the experimental profile is given by the dotted curve; the dashed line shows the background contribution. In (a) the theoretical values of the parameters are $U(^1G_4)=5.8$ eV, $g=0.41$ eV, while in (b) they are $U(^1G_4)=3.4$ eV, $g=0.41$ eV. The inset in (a) shows the experimental Ag loss spectrum (Ref. 21).

spectrum.

Despite the success of the Cini-Sawatzky model (CSM) in interpreting Auger spectra our recent results[1] for metallic Au showed that the basic CSM framework does not correctly describe the relationship between spectral profile and kinetic energy. In our analysis of the $N_{67}O_{45}O_{45}$ transitions of Au, the spin-orbit and band degeneracy were treated by a matrix theory,[7] able to account for multiplet terms exactly. We showed that setting the value of the only free parameter in the analysis, $U(^1G_4)$, at 3.4 eV gave a theoretical line shape in very good agreement with experiment but shifted by 1.2 eV to lower binding energy. Increasing $U(^1G_4)$ to 4.6 eV to recover the position gave a poor line shape. This discrepancy has been attributed to the neglect of interatomic ("off-site") correlation effects[8] in the CSM formalism. Model calculations[9] using a distance-dependent Coulomb repulsion have shown that the effect of off-site interactions is to increase the binding energy of the two-hole final state with respect to the position predicted by CSM. We note that similar discrepancies between experimental and theoretical Auger profiles to those noted here for Ag and earlier for Au (Ref. 1) have also been observed in carbon compounds.[10,11] This suggests that off-site contributions may play a role in these systems.

Our purpose in this work is to establish the extent to which the Cini-Sawatzky theory can satisfactorily describe correlation effects in the final state of Ag $M_4N_{45}N_{45}$ Auger transitions. We begin by applying a generalized CSM;[7,1] for Ag, the presence of the surface plasmon (3.68 eV) requires a further extension of the theoretical treatment, to allow for a dynamical plasmon-Auger-hole coupling.

A. Matrix formulation

Extending the CSM[2-4] to deal with band degeneracy and spin-orbit interaction,[7] the Auger spectrum for each of the two core-level contributions is given by

$$A(\omega)=\sum_{\lambda_J}\sum_{J} I(\lambda_J)\frac{1}{\pi}\mathrm{Re}[\Phi(\omega)]_{\lambda_J\lambda_J}\ , \qquad (1)$$

where λ_J labels the atomic intermediate-coupling (IC) two-hole eigenvectors which span a total J subspace

$$|\lambda_J\rangle=\sum_{SLJ}\langle SLJ|\lambda_J\rangle|SLJ\rangle\ . \qquad (2)$$

In Eq. (1), $I(\lambda_J)$ are the atomic IC transition rates for different λ_J, while $[\Phi(\omega)]_{\lambda_J\lambda_J}$ is the diagonal matrix element of the Green's operator $\Phi(\omega)$ in the λ_J representation,

$$\begin{aligned}\Phi(\omega)&=-i(\omega+H-i0^+)^{-1}\\&=[\mathbb{1}+i\Phi^{(0)}(\omega)\mathbf{U}]^{-1}\Phi^{(0)}(\omega)\ ,\end{aligned} \qquad (3)$$

where $H=H_0+H'$ is the sum of a noninteracting term H_0 describing the spin-orbit-resolved band structure, and an interacting part H', which accounts for correlation effects in the final state,

$$H'=\sum_{SLJM}U(SL)|00SLJM\rangle\langle 00SLJM|\ .$$

According to (3), $\Phi(\omega)$ can be expressed in terms of the noninteracting resolvent $\Phi^{(0)}(\omega)$ and the screened interaction operator $\mathbf{U}$. In the $|SLJM\rangle$ picture,

$$\langle SLJ|\mathbf{U}|S'L'J'\rangle=U(SL)\delta_{SS'}\delta_{LL'}\delta_{JJ'}\ . \qquad (4)$$

For a d^8 configuration in the gas phase, $U_0(SL)=F^0+f_{SL}(F^2,F^4)$, where $F^{0,2,4}$ are Slater's integrals and f_{SL} is well known.[12] In the solid state, F^0 is substantially reduced, whereas F^2, F^4 retain approximately their atomic values.[13] The differences $U(SL)-U(S'L')$ depend only on F^2 and F^4 and we can write $U(SL)=U(^1G_4)+f'_{SL}(F^2,F^4)$, with $f'_{S=0\ L=4}(F^2,F^4)=0$. In the following, as for the case of Au,[1] we take atomic values for F^2,F^4 and use the screened term $U(^1G_4)$ as a free parameter.

In the same $|SLJM\rangle$ basis, $\Phi^{(0)}(\omega)$ can be related via angular coefficients to the convolution of one-particle local densities of states, in the jj coupling. Then, for closed bands, Eq. (3) is exactly solvable, and by Eqs. (2) and (4) we can calculate $A(\omega)$ in Eq. (1) (see Ref. 7 for details).

B. Dynamical screening effects

Cini and D'Andrea[14] have studied how the coupling of Auger holes and plasmons can affect the Auger line shape; they showed that if one describes the plasmon dynamics by one efficient mode then the model can be solved exactly for closed bands in terms of a continued-fraction technique. Their model Hamiltonian, for a single-*s* band Sawatzky model, is

$$H=\left[H_0+U_0\sum_i n_{i+}n_{i-}\right]+[\omega_p b^\dagger b]+\left[2g_0\sum_i n_{i+}n_{i-}+g_0\sqrt{2}\left[1-\sum_i n_{i+}n_{i-}\right]\right]\times(b^\dagger+b)\ , \qquad (5)$$

where ω_p is the plasma frequency (3.68 eV for Ag), g_0 is the plasmon coupling constant, $b^\dagger$ creates a plasmon excitation, and U_0 is the intratomic interaction term with its bare, gas-phase value. In Ref. 14 it is shown that the two-hole Green's function can be calculated exactly in terms of a continued fraction which accounts for the infinite plasmon replicas of the spectrum. The *n*th replica is described by the shifted Green's function $\Phi_n(\omega)=\Phi(\omega-n\omega_p)$, where $\Phi(\omega)$ is the no-plasmon two-hole Green's function; $\Phi(\omega)$ is calculated in terms of a canonically transformed electron Hamiltonian $\mathcal{H}$

$$\mathcal{H}=H_0+U_d n_{0+}n_{0-}-\frac{2g_0^2}{\omega_p}\ , \qquad (6a)$$

$$U_d=U_0-4(\sqrt{2}-1)\frac{g_0^2}{\omega_p}=U-\frac{g^2}{\omega_p}\ , \qquad (6b)$$

where $g=(2-\sqrt{2})g_0$ is the effective coupling and U is the interaction parameter in the static limit of the theory ($\omega_p\rightarrow\infty$), when the usual CSM is recovered. In other words, the problem is now formulated in terms of renormalized U_d and g, used as adjustable quantities: with respect to static theory, there is an extra free parameter, namely g. This "dynamical" theory of Auger decay may have a nontrivial effect on the line shape due to the additional energy channel now available: variations of the plasma frequency ω_p, the interaction U_d, and bandwidth *W*, allow two-hole resonances to acquire extra broadening and eventually delocalize into the continuum. The formulation also fixes the ranges of applicability of the "static" Cini-Sawatzky theory, and has been applied to the analysis of the Auger spectrum of graphite,[15] generalizing the treatment to degenerate bands: in the case of band degeneracy, Eq. (6b) for the matrix interaction $\mathbf{U}_d$ in the *SLJ* basis becomes[15]

$$\mathbf{U}_d=\mathbf{U}-\frac{g^2}{\omega_p}\mathbb{1}\ .$$

As for the static case, the differences $U_d(SL)-U_d(S'L')$ are not affected by the renormalization procedure and all $U_d(SL)$ can be referred to $U_d(^1G_4)$. Then, also for degenerate bands, we have only $U_d(^1G_4)$ and g as free parameters. We follow the same approach as in Refs. 14 and 15 and consider only the first plasmon replica of the spectrum, which amounts to truncating the continued-fraction matrix solution. We defer the discussion of the contribution made by off-site interactions to Sec. V.

IV. PRELIMINARY CONSIDERATIONS

In order to apply the theoretical formalism described above to the $M_{45}N_{45}N_{45}$ Auger spectrum of Ag we first need to determine the final-state multiplet splittings and intensities, the one-particle (*j*-resolved) DOS, the spectral broadening, and the background of scattered electrons accompanying the experimental spectrum. We consider each of these contributions in turn.

(i) Due to the open 5*s* shell, the $M_{45}N_{45}N_{45}$ Auger spectrum of atomic Ag (Ref. 16) exhibits additional multiplets compared to the metallic state.[6] We found that splittings derived from atomic optical data[17] are in good agreement with the profile of these transitions for free atoms. Interpreting these splittings in terms of a d^8s^1 configuration we obtained values of the Coulomb integrals and spin-orbit coupling parameter of $F^2=7.67$ eV $F^4=5.51$ eV, and $\xi_{4d}=0.21$ eV, respectively. These values were then used to determine the multiplet splittings of the d^8 configuration in the metallic phase shown in Table I.

(ii) The relative intensities of the components, also given in Table I, have been calculated previously.[6,18] For the fourth-row elements following Rh, the 4*d*-band binding energy in the presence of a core hole is greater than the 3*d* spin-orbit splitting and so $M_4M_5N_{45}$ Coster-Kronig processes are not energetically possible. Since the transition rate for M_4M_5V processes is very low, the $M_5N_{45}N_{45}/M_4N_{45}N_{45}$ intensity ratio is expected to be given accurately by the M_5/M_4 ratio of initial-state holes. This quantity was taken from the 3*d* photoelectron cross section,[19] giving $I(M_5)/I(M_4)=1.45$, in good agreement with the experimental photoelectron intensity

TABLE I. Multiplet structure for a $4d^8$ configuration in Ag. The components are identified by the *LS* term which makes the largest contribution to the intermediate-coupling (IC) state. Energy splittings (relative to the $^1G_4$ component) were calculated using $F^2=7.67$ eV, $F^4=5.51$ eV, and $\xi_{4d}=0.21$ eV. The Slater's parameters were obtained by interpreting optical data (Ref. 17) in terms of a d^8s^1 configuration. Corresponding intensities for the M_4, M_5 subgroups are taken from Ref. 6.

Eigen vector	Energies (eV)	Intensities	
		M_5	M_4
$^1S_0$	−3.05	0.13	0.22
$^1G_4$	0.0	1.00	1.14
$^1D_2$	0.32	0.24	0.88
$^3P_0$	0.38	0.11	0.09
$^3P_1$	0.41	0.24	0.37
$^3P_2$	0.90	0.58	0.32
$^3F_2$	1.71	0.40	0.37
$^3F_3$	1.90	0.41	0.61
$^3F_4$	2.35	1.00	0.10

results (1.47±0.05), the statistical value (6/4), and the experimental M_5NN/M_4NN intensity ratio (1.52) for atomic Ag.[16]

(iii) In order to apply the matrix formulation of the CSM we need *j*-resolved one-particle LDOS's. These were taken from the work of Christensen.[20] The binding energies of the centers of mass of the $j=\frac{3}{2}$ and $j=5.2$ eV subbands are at 5.8 and 5.2 eV respectively, with a corresponding mean level E_{4d} at 5.43 eV and an effective coupling ξ_{4d} of 0.23 eV, the latter in good agreement with our atomic estimate.

(iv) To simulate the inelastic background contribution we convoluted the theoretical curve with the experimental loss spectrum of Ag,[21] matching the sum of theoretical and background shape to the experimental curve in the structureless region at the high-binding-energy side.

(v) Concerning broadening contributions in the initial states, we note that the width of the M_{45} photoelectron lines is 0.30 eV in the metallic state (M_4M_5V Coster-Kronig rates are negligible), which is consistent with a measured lifetime in the atomic phase of 0.21 eV,[16] and the calculated phonon contribution of 0.12 eV.[22] In estimating final-state broadening contributions, both dispersion and lifetime factors must be considered. According to Ref. 23 the dispersion contribution Γ_d for a fcc structure can be estimated from $\Gamma_d = W^2/8U$, where W is the bandwidth. This gives $\Gamma_d \sim 0.25$ eV for Ag, which is significant and may obviously vary across multiplet components. Solid-state N_{45} holes can decay via $N_{45}N_{45}V$ and $N_{45}VV$ transitions giving a lifetime contribution to the broadening. For free-electron valence states the lifetime broadening increases with binding energy since the number of decay channels increases, and this gives a broadening of ~ 1 eV at the bottom of the band.[24] For Cu and Ag the lifetime has been estimated from x-ray photoelectron spectroscopy to be ~ 0.3 eV at the bottom of the *d* band.[25] For the $[4d^2]$ state, Auger vacancy transitions $N_{45}N_{45}$-$N_{45}N_{45}V$ and $N_{45}N_{45}$-$N_{45}VV$ can occur. These considerations lead us to expect a final-state lifetime broadening of the quasiatomic two-hole states of the order of ~ 0.6 eV. This is consistent with the final-state broadening of 0.5 eV observed in metallic Cd,[26] which may be attributed solely to lifetime broadening. These semiquantitative considerations suggest an *a priori* estimate of the total broadening of 1 eV. In our theoretical calculation we used a Lorentzian broadening of full width at half maximum (FWHM) $=0.8$ eV.

V. RESULTS AND DISCUSSION

In order to assess whether the off-site contributions which were found necessary in order to explain the Auger spectra of Au are also present in Ag, we apply the theory developed above, which neglects off-site effects, to the $M_{45}N_{45}N_{45}$ Ag spectrum shown by the dots in Fig. 1.

A. Comparison of CSM results with experiment

The theoretical CSM results are shown by the full curves in Fig. 1, in which the value of the free parameter, $U(^1G_4)$, is chosen as 5.8 and 3.4 eV in Figs. 1(a) and 1(b), respectively, and $g=0.41$ eV. We note that the plasmon coupling g causes the dynamical "U" values, U_d, to differ from the static values, U, by 0.05 eV (see Sec. III B) and for practical purposes we use $U=U_d$ in the following.

Figure 1 shows that it is not possible to obtain simultaneous agreement with the energy and profile of the Auger transitions by using a single value of the free parameter $U(^1G_4)$. It is however quite possible to achieve good agreement between the experimental and theoretical profiles provided the theoretical results are shifted 2.2 eV to lower binding energy. Good agreement with the observed energy of the transitions can also be achieved but only at the expense of significant disagreements in the profile [Fig. (1a)]. This is a similar result to that found for Au, where the discrepancy between the accurate profile and experiment was 1.2 eV.

Considering Fig. 1(a) in detail it is clear that the ^3F components, which make strong contributions at low binding energy in the spectrum of each group, are too narrow in the theoretical profiles. This indicates that $U(^3F)$ is smaller than assumed, causing these components to broaden and delocalize into the *d* band. The theoretical profile also fails to yield sufficient spectral intensity between the $M_5N_{45}N_{45}$ and $M_4N_{45}N_{45}$ groups and to predict the observed separation in the $M_{45}N_{45}N_{45}$ group between the strong $^1G_4$ component and $^1S_0$ component at high binding energy. All three of these discrepancies are corrected by the reduced on-site correlation energies used to generate the theoretical spectral profile shown in Fig. 1(b). This is our best theoretical Auger profile for Ag and it is not strongly sensitive to small variations (≈ 0.3 eV) in the "best-fit" value of the $U(^1G_4)$ parameter.

It is interesting to consider the role of dynamic screening effects[14,15] in our theoretical treatment of the Ag Auger spectrum. The inset in Fig. 1(a) shows the electron-energy-loss spectrum of Ag taken from Ref. 21. We find that dynamic effects make only minor contributions to the calculated spectrum for weak plasmon coupling and that increasing g_0 causes the theoretical profile to deteriorate rapidly. In particular, it is not possible to add intensity to the theoretical profile between the two groups in Fig. 1(a) by increasing the plasmon coupling. Our calculated background gives good agreement with the experimental results, which suggests that the plasmon contribution is mainly extrinsic in Ag. Although the theoretical profile shown in Fig. 1(b) is in good agreement with experiment it is not perfect. In particular the theoretical profile is slightly broader than experiment and the overall intensity of the $M_4N_{45}N_{45}$ group is slightly overestimated. Subtle processes like $N_{45}N_{45}$-$N_{45}N_{45}V$ and $N_{45}N_{45}$-$N_{45}VV$ transitions which are not included in the theoretical treatment could be responsible for these discrepancies.

We have established that the CSM is able to predict a good profile for the $M_{45}N_{45}N_{45}$ Auger spectrum of Ag at the "wrong" energy. This is a similar result to that found for Au, but much larger. As in the case of Au, we can eliminate surface effects and dynamic screening effects as sources of this discrepancy.

B. The role of the off-site interactions

We now consider the role of off-site interactions in Ag. To study qualitatively how they can affect the line shape, a single-*s*-band extended Hubbard model was studied in Refs. 8 and 9, by considering the following Hamiltonian,

$$H=H_0+\sum_{R} U_{R\uparrow}n_{R\downarrow}+\sum_{R\neq R}\mathcal{U}(|R-R'|)n_{R\uparrow}n_{R\downarrow}\ . \tag{7}$$

For a two-hole state this gives rise to a repulsive hydrogenlike problem on the lattice, which can be solved by a perturbative approach to yield an extra self-energy contribution which contributes a complex, weakly energy-dependent, shift $s(\omega)$ to the Cini-Sawatzky two-hole Green's function. The analytical expression for $s(\omega)$ to first order in $\mathcal{U}$, and in the dispersionless limit[8,9] for the two-hole momentum is

$$s(\omega)=\frac{\sum_{R\neq 0}\Phi^0_{00;0R}\,\mathcal{U}(|R|)\Phi^0_{00;0R}}{\sum_{R\neq 0}\Phi^0_{00;0R}\,\Phi^0_{00;0R}}\ ,$$

$$\Phi^0_{00;0R}=S^0_{00}(\omega)\otimes S^0_{0R}(\omega)\ , \tag{8}$$

in terms of the off-diagonal one-hole Green's function $S^0_{0R}(\omega)$. According to this description and as shown for a model potential in a simple cubic lattice, it was suggested in Refs. 8 and 9 that due to off-site interactions, both position and shape can be matched simultaneously, which is not the case for the Cini-Sawatzky treatment of Au and Ag. The shift required to correct CSM treatment of the Auger spectrum of Ag [Fig. 1(b)] is ~2.2 eV, which is 1 eV greater than for Au. Intuitively one would expect approximatively the same value for both metals.

In order to understand this different energy shift for Au and Ag, and how this relates to the effect of off-site interactions, we observe that although similar in many respects, Au and Ag have a different bandwidth W. Whatever the detailed screening mechanism in both metals, it is reasonable to assume that it leads to a similar value of the two-hole interaction in Ag and Au: this is certainly true for the intrasite multiplet terms $U(SL)$. However, the Auger spectra are different in character due to the different U/W ratios of the two metals. The different bandwidth must also affect the off-site contribution, as the relevant quantity is the off-site-interaction/W ratio. For example, in a simple Thomas-Fermi picture and assuming one s electron per atom, one concludes that two holes on nearest-neighbor sites in Ag and Au experience a similar interaction u, which is a consistent fraction of the corresponding on-site value U. Also, this u value would be almost independent of the multiplet term, because it originates from an averaging over degenerate orbitals. Now according to the U/W ratio, in Ag the two-hole states will be more localized in character than in Au and thus they will experience on average a greater off-site contribution. This should result in a *larger shift in Ag than in Au,* as observed. Our previous[8,9] treatment of off-site terms was essentially first order, Eqs. (7) and (8), in the off-site interaction or, more precisely, in the u/W ratio. This resulted in a satisfactory explanation for Au, where u/W was assumed small. For Ag, where u/W is greater, we expect a first-order treatment in u/W to be insufficient. For this reason, a higher-order treatment of off-site interactions is currently under investigation[27] and preliminary results are in line with our preceding discussion.

VI. CONCLUSIONS

We have shown that the off-site contributions to electron correlation which were found necessary to give good agreement with both the energy and the spectral profile of the $N_{67}O_{45}O_{45}$ Auger spectra of Au are also required to explain the $M_{45}N_{45}N_{45}$ Auger spectra of Ag. The contribution of off-site correlation effects to the binding energy of the d^2 hole states is significantly greater in Ag than in Au, and we conclude that this is due to the different off-site-interaction/bandwidth ratio for the two metals. More speculatively, we suggest that a higher-order treatment of the off-site interaction and its relationship to the bandwidth ratio will give insight into the understanding of the electron screening process, its degree of localization, and electron correlations.

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