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An Improved Real-Space Genetic Algorithm for Crystal Structure and Polymorph Prediction

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Existing Genetic Algorithms for crystal structure and polymorph prediction can suffer from stagnation during evolution, with a consequent loss of efficiency and accuracy. An improved Genetic Algorithm (GA) is introduced herein which penalizes similar structures and so enhances structural diversity in the population at each generation. This is shown to improve the quality of results found for the theoretical prediction of simple model crystal structures. In particular, this method is demonstrated to find three new zero-temperature phases of the Dzugutov potential that have not been previously reported.

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I. INTRODUCTION

Genetic algorithms (GAs) are emerging as a useful tool in the theoretical prediction of crystal structures (see Abraham and Probert¹, and references therein)²⁻⁴. During a GA calculation it is possible that the system will *stagnate*. When stagnation occurs, one or more local minima dominate the search and the method is unable to find the global minimum solution. In this communication we improve the convergence to the global minimum solution of the CASTEP-GA¹ through the use of a fitness function which is able to differentiate structures during the course of a GA minimization.

Binary-encoded GAs such as the method of Hart et al.⁵, Blum et al.⁶ are able to directly compare the binary strings that make up their population members and determine if two populations members are the same. In this way it is possible to remove any highly prevalent local minimum from the population, and prevent its creation in future mating operations. While this method is not possible in the framework of the CASTEP-GA, we have developed an alternative approach that significantly reduces the stagnation rate and also forces the system to explore new minima. This alternative approach is also broadly transferable to a wide range of other GAs.

II. METHOD

Our GA method¹ is a real-space encoded technique for crystal structure prediction which takes advantage of the periodicity of the simulation supercell to improve the speed and accuracy of convergence to the global minimum free-energy crystal structure. There is a *population* of structures (or *members*) which are bred together to produce new members, such that with each subsequent *generation* the population evolves in an attempt to determine the global minimum structure. The *fitness function* of the GA is used to determine how good (“fit”) a structure is and this is then used to weight the probability of survival of that structure and its probability to produce offspring.

While this method has been very successful in the past, we wanted to reduce the stagnation rate and thereby improve the quality of the solutions produced during a GA structure search. Since this is a real-space based approach it is not possible to directly compare the atomic co-ordinates of two popu-

lation members to determine if they are the same structure. In our previous work¹, the enthalpy of the structure was used to calculate the fitness. In this work, we propose augmenting this fitness function with an additional function which is able to determine the similarity of two structures. We shall illustrate the effectiveness of this new approach by first studying the Lennard-Jones crystals for comparison with our previous results and then the high pressure phases of the Dzugutov potential⁷.

The enthalpy-based fitness function is

$$f_i = \frac{[1 - \tanh(2\rho_i - 1)]}{2} \quad (1)$$

with the variable ρ_i being defined by

$$\rho_i = \frac{V_i - V_{min}}{V_{max} - V_{min}} \quad (2)$$

where V_{max} is the enthalpy of the highest enthalpy member of the population, V_{min} is the enthalpy of the lowest enthalpy member and V_i is the enthalpy of the member i being considered. The fitness of each member i is f_i and this is a function which varies between zero and one. Population members with a fitness close to zero are less “fit”, and members with a fitness close to one are more “fit”. Population members are then selected (using roulette-wheel selection) for reproduction or are removed from the population based on this fitness value.

This should mean that only fit members are selected to remain in the population, or are allowed to breed (*crossover*). It is often very likely that during the course of a calculation multiple copies of population members are made. In a bit-string represented GA duplicate members are very easy to spot but in a real-space encoded GA it is very hard to tell if two members are the same during the course of a calculation, since the crystal structure may be orientated or translated in any way within the simulation cell (due to use of periodic boundary conditions). This is even harder if the simulation cell parameters are also allowed to vary during the course of a calculation.

Hence we need a simple measure of structural similarity so that we can detect when duplicate structures exist within a population. Whilst this is encouraging from the point of view of ultimate structural convergence, in the early stages of the GA minimization we want to ensure as much structural diversity as possible to enable a broad search of possible solutions and so we want to penalise similar structures.

Since we are using this routine to differentiate between like and unlike structures, rather than any form of comprehensive structural analysis, we can simplify this comparison somewhat. If we are performing a calculation in which we allow the number of atoms to vary, then we can make an educated guess that two structures with different numbers of atoms are different (or rather in this case any offspring produced in the crossover procedure will have a greater number of degrees of freedom to explore the potential energy surface), so we will have no need to compare these structures. We also do not need to compare each structure with all other structures, since we are merely trying to prevent stagnation rather than give a definitive structural comparison, and so we can simply compare all structures with the minimum enthalpy structure which has the same number of atoms as itself that exist in the current generation. We will define a comparison function between structures which returns zero if the structures are the same and one if the structures are suitably dissimilar. We also want to keep the fact that lower enthalpy structures are “better” than higher enthalpy ones, so we further weight the value that any given structure has by the value of f_i of the fittest member in that “set” which is made up of members with the same number of atoms. Here we define our improved fitness function as

$${}^j f'_i = (1 - \omega) {}^j f_i + \omega {}^j f_{fit} \star \begin{cases} 1 & i \equiv fit \\ R(\Lambda(k_r)) & i \not\equiv fit \end{cases} \quad (3)$$

where the left-superscript j above denotes comparing between groups with the same number of atoms only, f_i is as defined in equation 1, w is a weighting value between zero and one and $R(\Lambda(k_r))$ is a function which compares member i of the set of atoms j with the fittest member in that set (as defined by equation 1). This means that the fitness of the fittest member of each group (${}^j f_{fit}$) will be unchanged from its enthalpy value, and all other values in the group will be scaled accordingly. If the value of the fitness weight, w , is set to 1 then the maximum value of ${}^j f'_i$ that any member could have is the same value of the fittest member of the group, ${}^j f_{fit}$. If w is set to zero then this function reduces to that given in equation 1. The comparison function $R(\Lambda(k_r))$ is

$$R(\Lambda(k_r)) = \frac{\sum_{k_r} |\Lambda'(k_r) - \Lambda(k_r)|}{\sum_{k_r} \Lambda'(k_r)} \quad (4)$$

where consideration of the spherically averaged scattering intensity leads to

$$\Lambda(k_r) = \Omega^2 \left[N \sum_{n=1}^N \rho'^2(n) + 2 \sum_{n=1}^N \sum_{m>n}^N \rho'^2(n) \rho'^2(m) J_0(\sqrt{3}\pi k_r |\mathbf{r}_n - \mathbf{r}_m|) \right] \quad (5)$$

which is positive-definite (and is based on the Debye scattering formula⁸). In equation 5, there are N ions within the simulation cell which has a volume Ω , $\rho'(n)$ is the scattering factor of ion n which has the atomic real-space co-ordinate

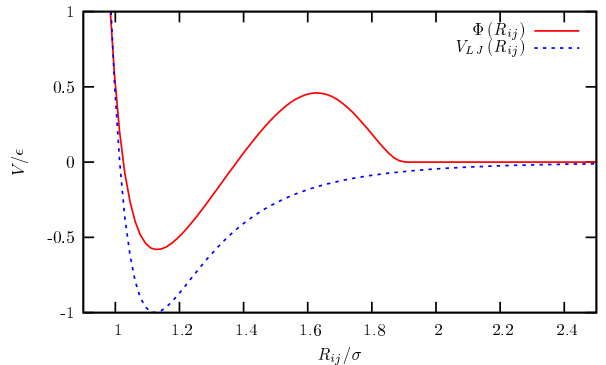


Figure 1: (Color online) Comparison of the Lennard-Jones and Dzugutov pair-potentials.

m	A	c	a	B	d	b
16	5.82	1.1	1.87	1.28	0.27	1.94

Table I: Table of parameters used in the Dzugutov potential (equation 6).

of \mathbf{r}_n , and $J_0(r)$ is a Bessel function. The function $\Lambda(k_r)$ of a population member i of each group j is tested against the function $\Lambda'(k_r)$ of the fittest member in the group j containing the same number of atoms as member i . Equation 4 is then used to compare these two functions and returns a single number between zero and one. In a variable-supercell calculation it is possible for this function to become greater than one when the structures are highly dissimilar, in which case we set the value of $R(\Lambda(k_r))$ to one.

III. RESULTS

The results presented here will use two different empirical potentials, the Lennard-Jones potential^{9,10} and the Dzugutov potential⁷ which is defined as

$$\Phi(R_{ij}) = \Phi_1(R_{ij}) + \Phi_2(R_{ij}) \quad (6)$$

where

$$\Phi_1 = \begin{cases} A(R_{ij}^{-m} - B) \exp\left(\frac{c}{R_{ij}-a}\right) & R_{ij} < a \\ 0 & R_{ij} \geq a \end{cases} \quad (7)$$

$$\Phi_2 = \begin{cases} B \exp\left(\frac{d}{R_{ij}-b}\right) & R_{ij} < b \\ 0 & R_{ij} \geq b \end{cases} \quad (8)$$

with the constants defined in table I. A comparison of these two potentials is shown in figure 1. The Dzugutov potential was originally formulated to simulate liquid systems, however it has also been shown to have some interesting solid phases¹¹, and can also be used to form quasi-crystals⁷.

The Dzugutov potential is designed such that the force on, and energy of, an atom moving within the potential go to zero at b/σ . As is reported in Roth and Denton¹¹ the Dzugutov potential has three known stable phases at varying pressures: BCC, the σ -phase and FCC.

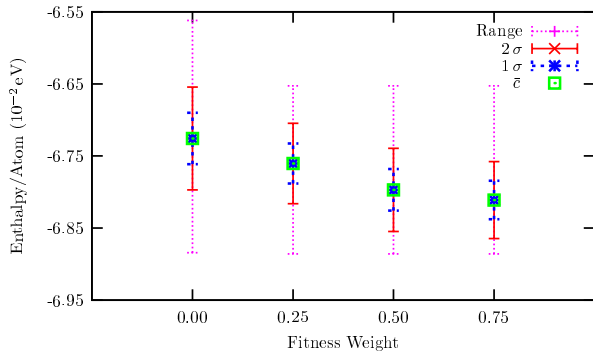


Figure 2: (Color online) Summary of the enthalpies of the different Lennard-Jones structures found for different fitness weights, which controls how much the comparison factor is considered during selection for update and crossover. The values for $w = 0.0$ are those from Abraham and Probert¹. All points are averaged over 15 independent calculations.

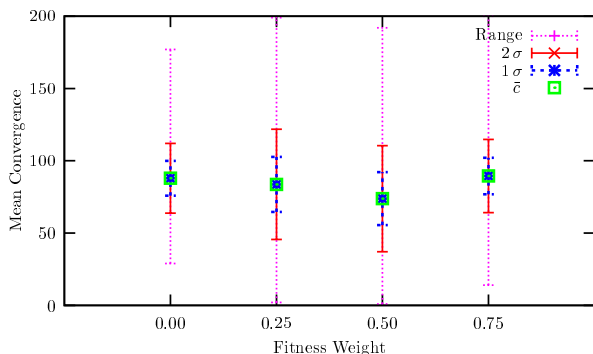


Figure 3: (Color online) Summary of the convergence times for the results shown in Figure 2. The values for $w = 0.0$ are those from Abraham and Probert¹. All points are averaged over 15 independent calculations.

A. Results from the Lennard-Jones potential

The use of the comparison factor in the selection procedure has a marked effect on the quality of the results produced as seen in Figure 2. While the global minimum structure is hexagonal close packed (HCP) this structure is nearly degenerate with the face-centred cubic structure (FCC) (with an energy difference of less than $0.1\%^{12}$). There are also a number of other stacking-fault structures which exist in-between FCC and HCP. The use of the comparison factor encourages the system to explore and hence escape from these local minima and find the HCP structure. With a fitness weight of $w = 0.75$ finding a HCP structure is much more likely.

The effect on convergence is interesting as seen in Figure 3. There is little increase in the mean number of generations required for convergence, although there is a greater spread in the values.

Figure 4 shows the results from a calculation performed with $w = 0.75$. We have included these results in particular because it shows the system going from an FCC structure to a HCP structure through two intermediate stacking-fault

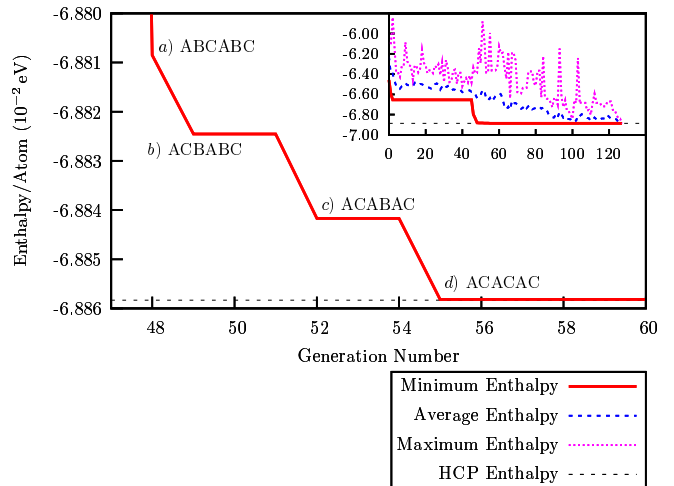


Figure 4: (Color online) Plot showing convergence to HCP minimum structure for a Lennard-Jones calculation with $w = 0.75$. The stacking patterns of the minimum enthalpy solutions are shown next to their appearance during the course of the simulation. The system converged to a HCP structure in 55 generations, and by the 127th generation all members were the same.

Fitness Weight	Pure HCP	Intermediate HCP-FCC	Pure FCC
0.00	0	6	0
0.25	3	3	0
0.50	3	6	0
0.75	6	3	0

Table II: Table comparing the number of each ordered structure type of the lowest enthalpy structure found (i.e. ignoring higher-enthalpy structures found during the course of a GA minimization) for different values of the fitness weighting factor w . Numbers given are out of a total of 15 calculations.

structures.

These results are summarized in table II. The results from $w = 0.00$ are those presented in Abraham and Probert¹.

B. Results from the Dzugutov potential

For results obtained using this potential an additional modification was made to the GA in the crossover step. Previously the atom-number could either be kept fixed or be allowed to vary in an unconstrained manner. For these Dzugutov calculations a third option was added, which is to allow the atom number to vary within an allowed percentage of the original number of atoms within the simulation supercell.

While this is not necessary in a fixed-cell size/shape calculation, for a variable-cell calculation it is essential. Without this constraint it would be possible for the number of atoms to keep decreasing with the cell getting smaller and smaller until the minimum image convention is violated, at which point the calculation will stop. It might also allow a calculation to keep adding atoms at the crossover stage and then allow the

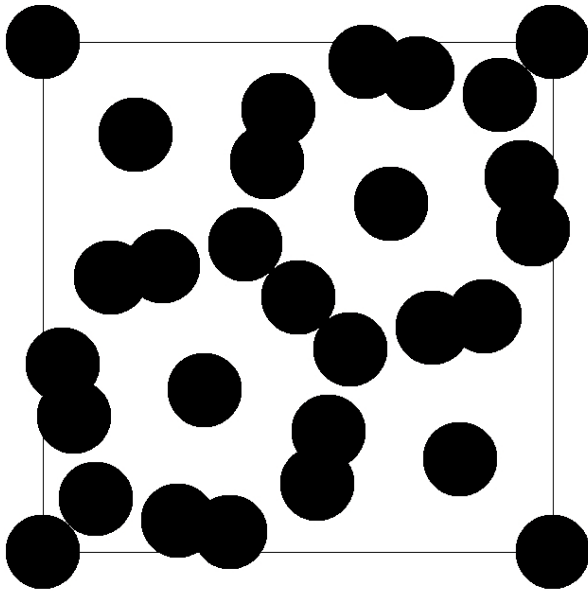


Figure 5: The unit cell of the Dzugutov potential σ -phase looking down the $[00\bar{1}]$ direction.

Pressure (MPa)	Lowest Enthalpy Phase \ddagger	Number of Each Phase Found				Lower Enthalpy Phase *
		Higher Enthalpy Phase	BCC	σ	FCC	
0	BCC	13	8	1	0	0
50	BCC	2	16	1	0	3
100	σ	1	9	11	0	1
150	FCC	1	0	0	15	6

\ddagger Data taken from Roth and Denton¹¹.

* Where the term ‘‘Lower Enthalpy’’ refers to having lower enthalpy than the phase in column 2.

Table III: Summary of results for 62-atom variable-cell, constrained variable-atom-number calculations. 22 independent GA calculations were performed at each pressure.

cell to grow to accommodate them. In this way the calculation would increase in size and take a longer and longer time for each minimization step. This percentage cut-off keeps the advantages of a variable atom-number calculation without these problems.

It is already known that the Dzugutov σ -phase has a complicated 30-atom unit cell (see Figure 5) and so all calculations had to have at least this many atoms. To prevent any bias of the final results, we started each run with 62 atoms in the unit cell and allowed the number of atoms to vary, in order to have an unbiased search of a large enough phase space.

A summary of the Dzugutov results is given in table III. Calculations were performed at four pressures, 0 MPa, 50 MPa, 100 MPa and 150 MPa which allows each of the three structures suggested by Roth and Denton¹¹ to be the most stable at at least one point during the experiment.

As can be seen in table III a number of GA minimizations

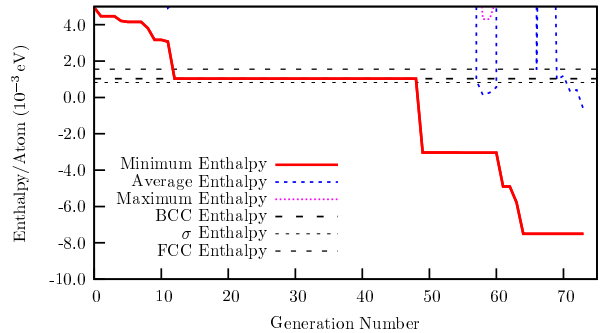


Figure 6: (Color online) Convergence plot of a variable-atom, variable-cell calculation, starting from 62 atoms. This gives rise to a previously unknown phase (labeled as phase ‘‘a’’ in Figure 8). The inset shows the complete calculation. The minimum-enthalpy structure found has 65-atoms and is shown in Figure 7.

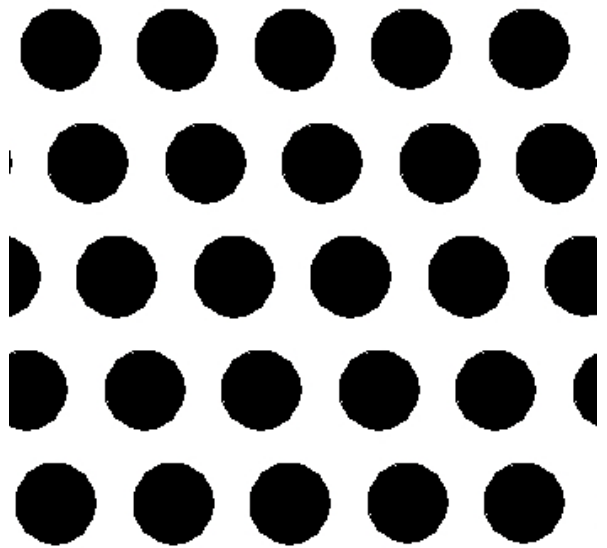


Figure 7: The structure of the new phase ‘‘a’’, a 65-atom phase found in generation 64 of the calculation shown in Figure 6.

found structures with a lower enthalpy than the previously reported minimum enthalpy structure. In total three distinct new structures were found. A plot showing the progress of a GA minimization down to the new lowest-enthalpy structure found is shown in Figure 6 with the structure itself shown in Figure 7.

A plot comparing the radial distribution functions of all the known and unknown phases of the Dzugutov potential is shown in Figure 8, as well as the HCP phase. The three new phases found are all significantly different from the established phases of this potential. Examination of these phases suggests that the simulation cells correspond to primitive cells and not supercells, but attempts to further characterize these structures by space group have so far been unsuccessful. The atomic co-ordinates of these structures are available online¹³ as supplementary material.

A plot showing the energy-volume curves for the six phases

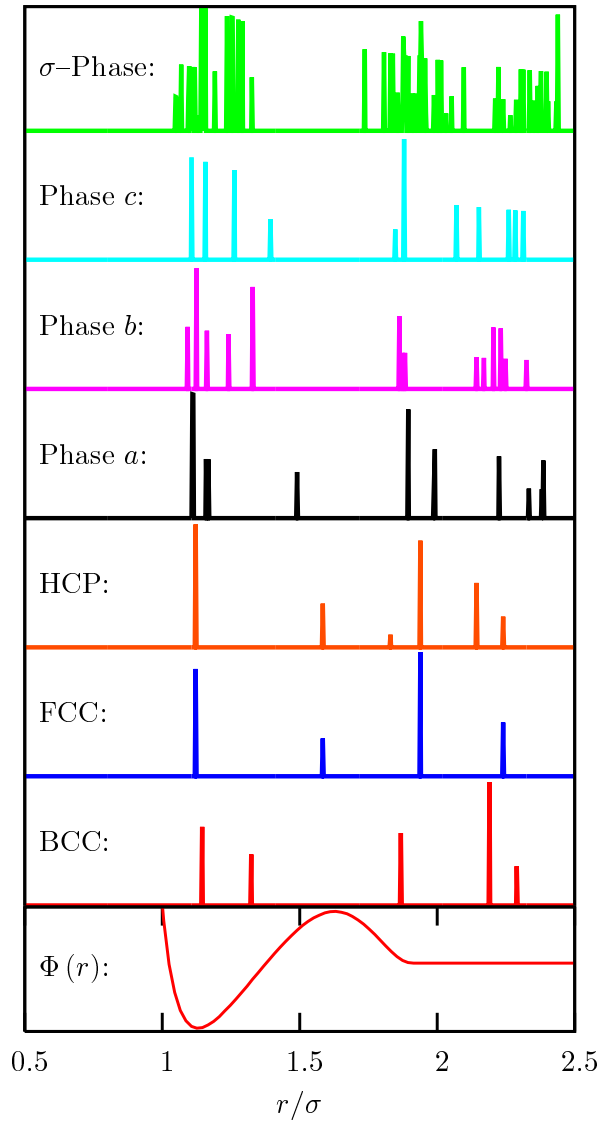


Figure 8: (Color online) Comparison of the radial distribution function, $g(r)$, for the distinct lower-enthalpy structures found with BCC, FCC, HCP and the σ -phase. The Dzugotov Potential is also shown.

of the Dzugotov potential found in the course of this study is shown in Figure 9. Phase “a” is the most stable phase at all positive pressures.

IV. CONCLUSIONS

In this paper we have developed a novel fitness function that combines a traditional approach to fitness based upon en-

thalpy, with a simple structural comparison factor to find new, more stable crystal structures within a GA for crystal structure prediction. This method penalises the presence of similar structures within the population which prevents the GA stagnating in some local minimum. The GA method itself was also extended to allow both the simulation supercell and the

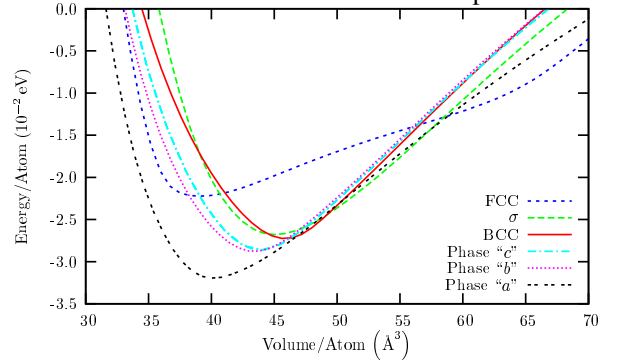


Figure 9: (Color online) Energy-Volume curve for the Dzugotov potential showing the three new phases calculated at zero pressure. The curves for the σ -phase and structures “a”, “b” and “c” were calculated assuming an isotropic expansion.

number of atoms within that supercell to vary. The number of atoms must only be varied within fixed limits to prevent the system size becoming too large or too small.

Studies using the Lennard-Jones potential showed the calculation progressing through the FCC local minimum and two other stacking-fault local minima before finding the HCP global minimum enthalpy structure. This was shown to be repeatable and efficient.

When this new GA was used to study phases of the Dzugotov potential at different pressures all the previously reported zero-temperature phases were found, along with three new phases, one of which is the most stable phase at all positive pressures. These new structures are markedly different from the three previously-known phases. This clearly illustrates the power of this GA to find new crystal structures that were hitherto unexpected.

V. ACKNOWLEDGMENTS

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