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# Effects of Ge substitution on the thermoelectric properties and pseudogap characteristics of $\text{Fe}_2\text{VGa}$

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## Abstract

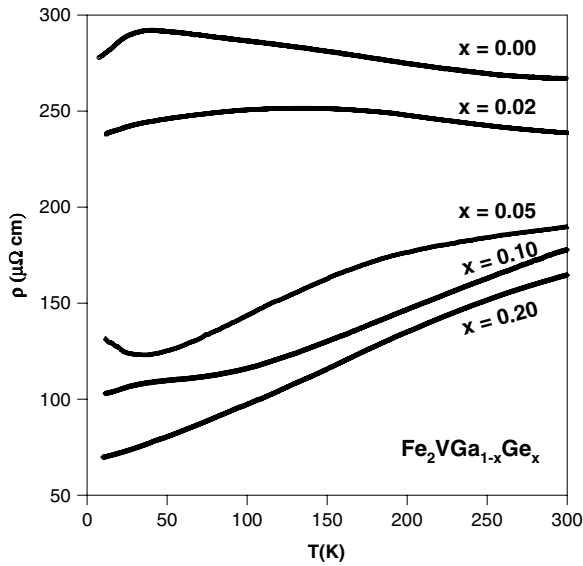
We report the effects of partial substitution of Ge onto the Ga sites of  $\text{Fe}_2\text{VGa}$  by measuring electrical resistivity, Seebeck coefficient and thermal conductivity as a function of temperature. It is found that Ge substitution effectively dopes electrons to the system and thus causes a dramatic decrease in the electrical resistivity. The Seebeck coefficient changes sign from positive to negative upon replacing Ga by Ge, which is in good agreement with a simple band filling picture. In addition, the magnitude of the Seebeck coefficient gradually increases and attains a maximum value of  $85 \mu\text{V K}^{-1}$  at around 120 K for  $\text{Fe}_2\text{VGa}_{0.9}\text{Ge}_{0.1}$ . Such a variation of Seebeck coefficient can be understood by means of rigid band-like shifting of the Fermi level across the pseudogap. The thermal conductivity is also reduced and a detailed analysis based on the Debye approximation indicates that the extrinsic disorder introduced by Ge substitution in  $\text{Fe}_2\text{VGa}$  has a minor contribution to the point defect scattering. Other lattice imperfections, such as antisite disorder, may be the main source for the point defect scattering which shows no systematic variation with Ge concentration. While the thermoelectric performance improves with the partial substitution of Ge, the largest figure-of-merit ( $ZT$ ) value among these presently investigated alloys is still an order of magnitude lower than the conventional thermoelectric materials.

## 1. Introduction

While Heusler-type intermetallics with the general formula  $\text{X}_2\text{YZ}$  (X and Y are transition metals and Z is an element from columns III–VI in the periodic table) commonly appear as metals [1], semiconducting-like behavior has been observed in  $\text{Fe}_2\text{VAl}$  and  $\text{Fe}_2\text{VGa}$ , as evidenced by their negative temperature coefficient of resistivity (TCR) [2, 3]. Such a negative TCR feature has been attributed to the appearance of a pseudogap in the vicinity of Fermi-level density of states (DOS), and these materials have been characterized as semimetals. Experiments such as nuclear magnetic resonance (NMR) and optical conductivity measurements further confirmed the existence of deep pseudogaps near the Fermi energy ( $E_F$ ) in both compounds [4, 5].

As proposed by Mahan and Sofo, materials with a sharp DOS feature around  $E_F$  would be good candidates

for thermoelectric applications [6]. In general, the energy conversion efficiency of a thermoelectric material is determined by the figure-of-merit ( $ZT$ ), which is given as  $ZT = S^2T/\rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity and  $\kappa$  is the total thermal conductivity. While trying to achieve good thermoelectric performance, the main difficulty is the need to minimize the thermal conductivity of materials while reducing their electrical resistivity. The strategy to optimize these two conflicting parameters usually involves the increase of charge carrier by doping and the enhancement of phonon scattering by introducing crystallographic disorder. In this study, we have studied the effect of partial replacement of Ga by Ge on the electronic properties of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  alloys by means of electrical resistivity, Seebeck coefficient and thermal conductivity measurements from 10 to 300 K. Altering the composition allows a change of these quantities, and results are



**Figure 1.** Electrical resistivity as a function of temperature for  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$ .

valuable to understand the influence of the substitutional effect on the electronic properties as well as the pseudogap feature of  $\text{Fe}_2\text{VGa}$ .

## 2. Experiment

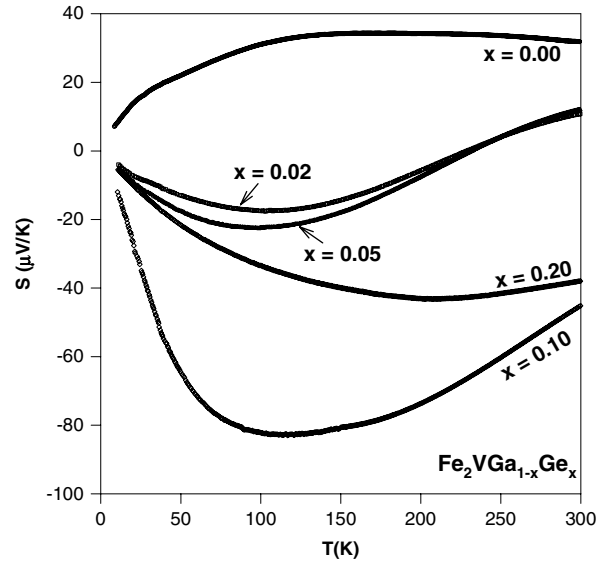
Polycrystalline  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  ( $x = 0, 0.02, 0.05, 0.10$  and  $0.20$ ) samples were prepared by an ordinary arc-melting technique. Briefly, a mixture of the appropriate amounts of high-purity elemental metals was placed in a water-cooled copper crucible and then melted several times under argon atmosphere in an arc furnace. The weight loss during melting is less than 0.5% for each composition. To promote homogeneity, these ingots were annealed in a vacuum-sealed quartz tube at  $600^\circ\text{C}$  for two days, followed by furnace cooling. A Cu  $K\alpha$  x-ray analysis on powdered samples from the annealed ingot was consistent with the expected  $L2_1$  structure, with no other phases evident in the spectrum.

Electrical resistivity data were obtained using a standard four-point probe method. Seebeck coefficient and thermal conductivity measurements were simultaneously performed in a closed-cycle helium refrigerator by the direct heat pulse technique. Further details about the experimental techniques can be found elsewhere [7]. All measured results presented in this work were performed during warming processes.

## 3. Results and discussions

### 3.1. Electrical resistivity

The evolution of electrical resistivity with Ge substitution of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  is presented in figure 1. It is apparent that the replacement of Ga with Ge atoms has the effect of reducing the electrical resistivity. Such a trend is attributed to the increase of electronic carriers via substitution, as Ge has one more electron in its valence shell than Ga. Based on a simple



**Figure 2.** Seebeck coefficient versus temperature in  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$ .

rigid-band scenario, the substitution of Ge onto the Ga sites would effectively dope electrons to the system and thus causes a upward shift of the Fermi level within the pseudogap region. Therefore the Fermi-level DOS increases with Ge content, as does the electrical conductivity. Such an interpretation was found to be consistent with the features of the Seebeck coefficient which will be discussed in the following section.

### 3.2. Seebeck coefficient

The temperature-dependent Seebeck coefficient of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  is shown in figure 2. For the stoichiometric compound, the measured  $S$  is positive over the entire investigated temperature range. Such an observation suggests that the dominant carriers are hole-type in  $\text{Fe}_2\text{VGa}$ , being consistent with the previous results. This is also in good agreement with the band structure calculations which revealed the existence of large hole pockets near the Fermi-level DOS of  $\text{Fe}_2\text{VGa}$  [8, 9]. Upon replacing Ga by Ge, the sign of  $S$  reverses, which is attributed to an increase of electrons, as expected from the nominal valences of Ga and Ge. Since the DOS within the pseudogap is very small and located in a rising portion of DOS, a slight change in the carrier concentration would result in an appreciable upward shift of the Fermi energy according to a simple rigid-band scenario. Such a shift reduces the hole pockets but enlarges the electron ones, leading to the n-type carriers dominating the thermoelectric transport in the Ge-substituted  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  alloys.

Another peculiar feature in  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  is the development of a broad minimum in  $S$  and the corresponding valley position moves to higher temperatures with increasing  $x$ . Similar observations have been noticed in other Heusler-type systems such as  $\text{Fe}_2\text{VAl}$  and  $\text{Fe}_2\text{TiSn}$  [10–13]. The upturn in  $S$  at high temperatures is very likely due to the contribution of thermally excited quasiparticles across their pseudogaps. Upon heating, intrinsic electrons and holes are excited. If the holes have a higher mobility than the electrons in these materials, the p-type carriers will eventually govern the thermoelectric

transport, leading to positive  $S$  values at high temperatures. In addition, the shifting of the  $S$  minimum toward higher temperatures with Ge content is associated with the increase of activated energy for the hole carriers thermally excited across the pseudogap. This is consistent with the band filling picture as the substitution of Ge onto the Ga sites of  $\text{Fe}_2\text{VGa}$  gradually shifts  $E_F$  to a higher part of the DOS.

For ordinary metals or semimetals, the sign and magnitude of  $S$  is usually described by the Mott formula:

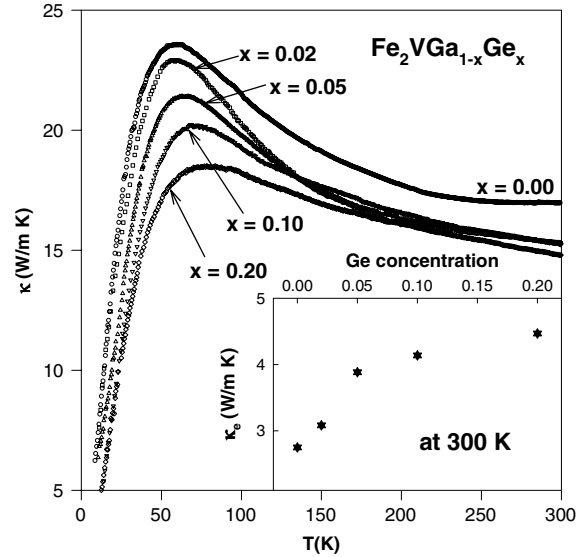
$$S = -\frac{\pi^2 k_B^2}{3e} \left( \frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right)_{E=E_F}. \quad (1)$$

Here  $e$  is the elementary charge,  $k_B$  is the Boltzmann constant and  $N(E)$  is the electronic DOS. It is generally true that a large Seebeck coefficient is brought about by a low  $N(E_F)$  combined with its steep slope,  $\partial N(E)/\partial E$ , in the vicinity of  $E_F$ . In this respect, the fact that  $\text{Fe}_2\text{VGa}$  is a p-type material while Ge-substituted alloys are n-type can be interpreted as a shift of  $E_F$  to a sharply rising portion of the conduction band DOS, giving a negative sign in  $S$  because of a positive value of  $\partial N(E)/\partial E$  at  $E_F$ . However,  $N(E_F)$  simultaneously increases with Ge substitution, which may effectively reduce the magnitude of  $S$ . As a consequence, the interplay between  $N(E_F)$  and  $\partial N(E)/\partial E$  would determine the sign and magnitude of  $S$ . For  $x \leq 0.1$  of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$ ,  $N(E_F)$  remains small and the factor of  $\partial N(E)/\partial E$  plays a crucial role, leading to an increase in the absolute value of  $S$  with Ge content. The maximum absolute value of  $S$  as large as  $85 \mu\text{V K}^{-1}$  at around 120 K was observed in  $\text{Fe}_2\text{VGa}_{0.9}\text{Ge}_{0.1}$ . On the other hand,  $N(E_F)$  becomes dominant with further Ge substitution, which tends to reduce the absolute value of  $S$ , as indeed found in  $\text{Fe}_2\text{VGa}_{0.8}\text{Ge}_{0.2}$ . Such an interpretation is also consistent with the marked reduction in electrical resistivity for this composition, attributed to the enlargement of electron pockets, as for the Fermi-level DOS.

### 3.3. Thermal conductivity

The observed temperature-dependent thermal conductivity  $\kappa(T)$  of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  is illustrated in figure 3. For all Ge-substituted samples, the room-temperature  $\kappa$  values are around  $16 \text{ W m}^{-1} \text{ K}^{-1}$ , relatively little affected with respect to the changes in the composition. At low temperatures,  $\kappa$  increases with temperature and a broad peak appears between 50 and 70 K. This is a typical feature for the reduction of thermal scattering in metals at low temperatures. A clear trend found in  $\kappa$  is that the height of the low-temperature peak gradually reduces with increasing the substitution level. This phenomenon is associated with a strong enhancement in the phonon scattering due to Ge substitution for Ga. We have a similar observation in the low-temperature thermal conductivity in the study of  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$  [14].

In general, the total thermal conductivity for ordinary metals or semimetals is expressed as a sum of electronic and lattice terms. The electronic contribution of heat transport can be estimated by the Wiedemann–Franz law:  $\kappa_e \rho / T = L_0$ . Here  $\rho$  is the dc electrical resistivity and the Lorentz number  $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ . The electronic contributions



**Figure 3.** Temperature dependence of the total thermal conductivity in the  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  alloys. The inset shows the plot of room-temperature electronic thermal conductivity versus Ge concentration estimated from the Wiedemann–Franz law.

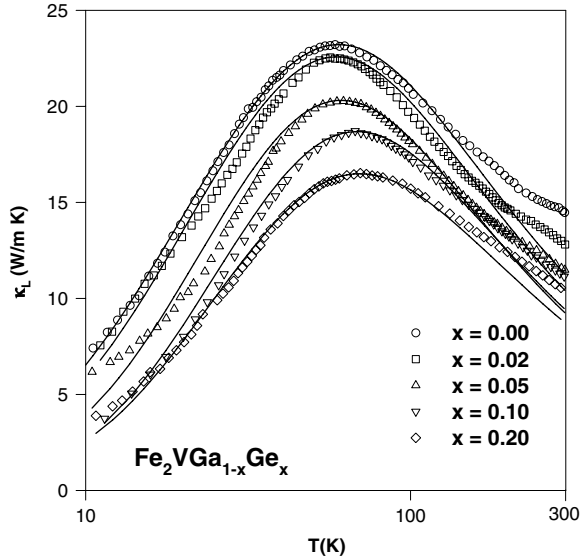
to the total thermal conductivity at room temperature (300 K) for this series of compounds, estimated from the Wiedemann–Franz law, are shown in the inset of figure 3. The result indicates that the total thermal conductivity is mainly associated with the lattice phonons rather than the charge carriers. In order to explore the influence of Ge substitution on the phonon scattering processes and the origin of the reduction in  $\kappa_L$ , we modeled the temperature-dependent  $\kappa_L$  using the Debye approximation. In this model  $\kappa_L$  is written as [15, 16]

$$\kappa_L = \frac{k_B}{2\pi^2 v} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D} \frac{x^4 e^t}{\tau_p^{-1} (e^t - 1)^2} dt, \quad (2)$$

where  $t = \hbar\omega/k_B T$  is dimensionless with  $\omega$  being the phonon frequency,  $\hbar$  is the reduced Planck constant,  $k_B$  is the Boltzmann constant,  $\theta_D$  is the Debye temperature,  $v$  is the average phonon velocity and  $\tau_p^{-1}$  is the phonon scattering relaxation rate. Here  $\tau_p^{-1}$  is the combination of three scattering mechanisms and can be expressed as

$$\tau_p^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 \exp\left(-\frac{\Theta_D}{3T}\right). \quad (3)$$

Here the effective grain size  $L$  and the coefficients  $A$  and  $B$  are fitting parameters, and  $\omega$  and  $v$  again represent the phonon frequency and average phonon velocity, respectively. The terms in equation (3) are the scattering rates for the grain-boundary, point defect and phonon–phonon umklapp scattering, respectively. In general, the grain-boundary scattering dominates the low-temperature  $\kappa_L$  while the umklapp process is important at high temperatures. The point defect scattering, on the other hand, has a strong influence on the appearance of the shape and position of the phonon peak occurring in the intermediate temperature regime. Taking  $\theta_D = 310 \text{ K}$  given from the specific heat measurement for



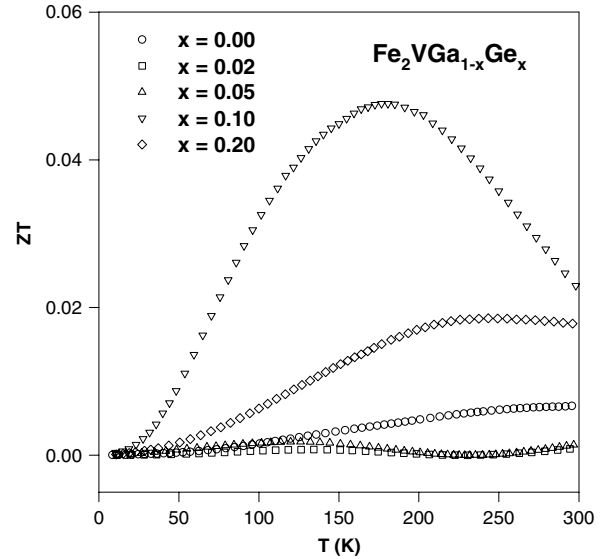
**Figure 4.** Lattice thermal conductivity for  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  versus temperature. The solid lines represent the calculation based on equations (2) and (3).

**Table 1.** Fitting parameters of the lattice thermal conductivity for  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  determined from equations (2) and (3).

Alloy	$v/L$ ( $10^9 \text{ s}^{-1}$ )	$A$ ( $10^{-43} \text{ s}^3$ )	$B$ ( $10^{-19} \text{ K}^{-1}$ )	$L$ ( $\mu\text{m}$ )
$\text{Fe}_2\text{VGa}$	0.97	1.40	1.60	3.09
$\text{Fe}_2\text{VGa}_{0.98}\text{Ge}_{0.02}$	1.15	1.30	1.90	2.61
$\text{Fe}_2\text{VGa}_{0.95}\text{Ge}_{0.05}$	2.00	1.13	2.40	1.50
$\text{Fe}_2\text{VGa}_{0.90}\text{Ge}_{0.10}$	3.33	1.03	2.30	0.90
$\text{Fe}_2\text{VGa}_{0.80}\text{Ge}_{0.20}$	3.33	1.28	2.30	0.90

$\text{Fe}_2\text{VGa}$  [17],  $\kappa_L$  can be fitted very well for  $T < 120$  K, shown as solid curves in figure 4. We have attempted to include the electron–phonon interaction in the calculations, but such an effort yielded no significant improvement to the overall fit. We thus conclude that electron–phonon scattering has a minor influence on the lattice thermal conductivity in these  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  alloys. It is noticed that the fitting curves deviate from the data points at high temperatures. The discrepancy may arise from radiation losses during the experiments, temperature dependence of the Lorentz number and the undetermined Debye temperatures for the substituted compounds.

All fitting parameters were tabulated in table 1. We notice an overall increase in the parameter  $v/L$  with increasing  $x$  value. Taking an estimated  $v = 3000 \text{ m s}^{-1}$  for all studied materials, the reasonable grain size  $L$  ranging from 0.9 to 3.1  $\mu\text{m}$  can be obtained. The umklapp coefficient  $B$  scatters around in these samples, presumably due to the unknown Debye temperature for these materials (except  $\text{Fe}_2\text{VGa}$ ). It should be noted that, even though the Debye temperature is a significant factor for the umklapp scattering rate, it only affects the fitting result at high temperatures. According to the model proposed by Klemens [18], the prefactor  $A$  would increase with the content of point defects in the low defect level. However, the value of  $A$  in the present case of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  does not



**Figure 5.** Figure of merit as a function of temperature for  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$ .

follow a consistent variation with  $x$ , similar to that observed in the off-stoichiometric  $\text{Fe}_2\text{VGa}_{1+x}$  alloys [19]. Such a result indicates that the extrinsic disorder introduced by Ge substitution in  $\text{Fe}_2\text{VGa}$  has a minor contribution to the point defect scattering. Rather, other lattice imperfections, such as antisite disorder, may be the main source for the point defect scattering which appears to have no systematic variation with Ge concentration.

### 3.4. Figure of merit

From the electrical and thermal transport properties presented above, one can estimate the thermoelectric performance of these  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  alloys. Figure 5 shows the figure of merit  $ZT$  as a function of temperature for various compositions. In the cases of  $x = 0.02$  and 0.05, the expected increase in  $ZT$  due to the promising reduction in  $\rho$  and  $\kappa$  is masked by their small  $S$  values. It is seen that the magnitude of  $ZT$  considerably increases with higher Ge substitution. A fourfold increase at room temperature and a tenfold enhancement at intermediate temperatures between  $\text{Fe}_2\text{VGa}$  and  $\text{Fe}_2\text{VGa}_{0.9}\text{Ge}_{0.1}$  are achieved. This is mainly due to the significant reduction in both  $\rho$  and  $\kappa_L$  together with the increase in the magnitude of  $S$  for a highly Ge-substituted level. In general, the substitution of heavier atomic elements is capable of reducing atomic vibration frequencies and hence the lattice thermal conductivity can be minimized. Indeed, a recent study on the isoelectronic compound  $\text{Fe}_2\text{VAl}$  has found an appreciable decrease in the lattice thermal conductivity with Ge substitution for Al, leading to a promising improvement of  $ZT$  up to 0.13 at room temperature [20]. Since Ge and Ga have similar atomic weight and radius, only minor suppression of  $\kappa_L$  is expected with Ge substitution for Ga in  $\text{Fe}_2\text{VGa}$ , as we did observe in this work. In this respect, heavier atoms' substitution is of great interest to study the possible enhancement of thermoelectric performance in this class of materials.



#### 4. Conclusions

A systematic study of the electrical and thermal transport properties of  $\text{Fe}_2\text{VGa}_{1-x}\text{Ge}_x$  ( $x = 0.00\text{--}0.20$ ) was performed. The reduction in the electrical resistivity as well as the variation of Seebeck coefficient with Ge substitution can be consistently interpreted as a rigid-band shift of the Fermi energy across the pseudogap. The analysis of lattice thermal conductivity suggests that the substitutional (extrinsic) disorder in  $\text{Fe}_2\text{VGa}$  has a relatively minor contribution to the heat conduction processes, and brings up the importance of the antisite (intrinsic) disorder responsible for the observed features. In this work, we clearly demonstrate that Ge substitution onto the Ga sites in  $\text{Fe}_2\text{VGa}$  represents a good opportunity for improving its  $ZT$  value, although these values are still small compared to the conventional thermoelectric materials. Apparently, the thermoelectric properties in these compounds have not been optimized and warrant further investigations.

#### Acknowledgments

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