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# $Gd^{3+}$ EPR PROBE OF THE DETERMINATION OF THE VALENCE STATES+

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## ABSTRACT

The theory of the $Gd^{3+}$ probe EPR technique is reviewed. This technique has been employed to investigate at 9.2 GHz the $Gd^{3+}$ EPR in 0.1 at. % GdS in TmS, 1 at. % GdTe in TmTe, and 1 at. % GdSe in TmSe. From the temperature dependence of the $Gd^{3+}$ EPR linewidth, we have concluded that Tm in TmS is trivalent with a singlet-ground-state. The temperature variation of the $Gd^{3+}$ linewidth in TmTe has been interpreted in terms of the "delocalization" of the extra electron "localized" around $Gd^{3+}$. From the linewidth and g-value data, we have shown that Tm in TmTe is divalent. The linewidth and the g-value of the $Gd^{3+}$ resonance in TmSe have been found to be independent of temperature. These striking results have been explained in terms of the "motional narrowing" effect attributed to the interconfigurational fluctuations of Tm in TmSe.

## INTRODUCTION

There has been much interest in recent years in the study of the valence states of the thulium ions in thulium monochalcogenides.[1-9] In this paper we report our results for TmSe, TmS and TmTe determined by the $Gd^{3+}$ impurity EPR (electron paramagnetic resonance). It has been shown that TmSe is an unusual mixed-valence-state material. According to Refs. 3 and 5, the thulium ions in TmSe are

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predominantly trivalent; the Mössbauer results have revealed[2] that the correlation time of the interconfigurational fluctuations between the $Tm^{2+}$ and $Tm^{3+}$ electronic configurations falls within $10^{-10}$ - $10^{-12}$ second. On the other hand, from their reflectivity data, Batlogg, et al.[6] concluded that the interconfigurational fluctuation does not exist in TmSe. However, the valence states of the Tm ions in TmS and TmTe are definite. From the lattice-constant[1] and the susceptibility measurements, Bucher, et al.[3] have determined that the Tm ions in TmS are almost trivalent, and from the optical and photoemission experiments, Suryanarayanan, et al[4] have concluded that Tm in TmTe is essentially divalent.

Since TmSe, TmS and TmTe are all cubic with the NaCl structure,[3] in comparison with the rare-earth monopnictides,[10] the cubic crystal-field is expected to split the Hund's rule ground-state of $Tm^{3+}$ ($J=6$) into various crystal-field states. This expectation has led to several unsuccessful attempts[3] to measure the crystal-field splittings in these compounds by neutron scattering, a technique which was successfully applied to rare-earth monopnictides.[11] According to these observations and the wide disparities between estimates of the $Tm^{2+}$ and $Tm^{3+}$ concentrations, it is evident that the thulium monochalcogenides form one of the most unique series of compounds for use in the study of unstable valence systems. Encouraged by the successful applications of the $Gd^{3+}$ probe EPR technique in the study of the crystal-field and exchange effects in thulium monochalcogenides,[12,13] we have investigated the $Gd^{3+}$ impurity EPR in TmS, TmTe, and TmSe. Our results[14] have confirmed that Tm is trivalent, divalent, and mixed-valent in TmS, TmTe, and TmSe, respectively. Hence this $Gd^{3+}$ probe technique can be used for studying the material with mixed valence as well.

In the next two sections we will review the theories pertinent to explain our experimental technique and data, and then will present the experimental results concerning the valence states of Tm in our Tm monochalcogenide samples.

## REVIEW OF THEORIES

In a recent paper, Sugawara, et al. have reported[12] their studies of some singlet-ground-state systems (Tm - and Pr - group VA intermetallic compounds). They obtained the exchange and crystal-field effects of these systems by observing the paramagnetic resonance of dilute $Gd^{3+}$ impurities used as a probe. (For succinctness, we term this method the "$Gd^{3+}$ probe EPR technique".) In this Sec., we will review the theories associated with this technique. A brief discussion of the narrowing of spectral lines by motions will be also presented.

## A. g-Shift Due to Gd-Host Exchange

We consider a paramagnetic system in which there are dilute $Gd^{3+}$ impurities (probes). If the exchange interaction between a $Gd^{3+}$ ion and the surrounding host magnetic ions is isotropic, then the Hamiltonian of the S-state $Gd^{3+}$ is written

$$\mathcal{H} = g_0\, \beta\, \vec{S} \cdot \vec{H} + \sum_j \mathcal{J}_j\, \vec{S} \cdot \vec{S}_j, \qquad (1)$$

where the first and second terms represent the Zeeman and exchange energies, respectively. $g_0$ is the g-value of the isolated $Gd^{3+}$ ion, $\beta$ is the Bohr magneton; $\vec{S}$ and $\vec{S}_j$ represent the spin of $Gd^{3+}$ and the j-th host magnetic ion surrounding the $Gd^{3+}$ ion in question, respectively; and $\mathcal{J}_j$ is the exchange interaction coefficient of $Gd^{3+}$ and the j-th host ion. Hutchings, et al.[15] have treated this problem, and they have shown that the $Gd^{3+}$ ion will exhibit a spin resonance with a g-value shifted from $g_0$. As long as the exchange energy is small compared to the crystal-field splittings, the g-shift can be expressed as[12,13,15]

$$\Delta g = \left( \frac{\lambda - 1}{\lambda} \right) \frac{\mathcal{J}(0)}{\beta^2}\, \chi_{CF}, \qquad (2)$$

with

$$\mathcal{J}(0) \equiv \sum_j \mathcal{J}_j. \qquad (3)$$

Here $\lambda$ and $\chi_{CF}$ are the Landé g-factor of the host magnetic ion and the crystal-field-only isothermal susceptibility of the host, respectively. When there are exchange interactions between the host magnetic ions Eq. (2) is modified.[16,12] However, for our purpose, Eq. (2) is a good approximation. Accordingly, the g-shift of $Gd^{3+}$ is proportional to the isothermal susceptibility of the host magnetic ion; and the exchange interaction coefficient $\mathcal{J}(0)$ can be obtained if we measure the g-shift of $Gd^{3+}$ at zero temperature, and if the isothermal susceptibility of the host, $\chi_{CF}$, is known. To date, Eq. (2) has been successfully utilized to interpret the temperature-dependent data of the wide variety of paramagnetic hosts (Tm and Pr monopnictides,[12] $PrPb_3$, TmCd, $PrIn_3$, and $PrAl_2$ compounds[17,18]).

## B. Theory of the Linewidth

In addition to the static magnetic field, $\vec{H}$, a $Gd^{3+}$ probe ion also experiences the exchange fields originating from the exchange interactions between the $Gd^{3+}$ ion and its neighboring host magnetic ions. When the spins of the host ions fluctuate, a fluctuating field at the site of the $Gd^{3+}$ ion results. This fluctuating field gives rise to an additional linewidth of the $Gd^{3+}$ EPR. Moriya and Obata[19] have investigated this problem in detail. Their theory predicts that the EPR linewidth of the magnetic impurity is proportional to the auto-correlation function of the spin fluctuations of the host magnetic ion $<S_j(t)S_j(0)>$. They concluded that the linewidth is approximately given by[19,20]

$$\Delta H = AkT\ (\chi_T - \chi_{iso}). \tag{4}$$

Here A is a proportionality constant, and $\chi_T$ and $\chi_{iso}$ are the isothermal and isolated susceptibilities of the host magnetic ion, respectively. (The isothermal susceptibility is the susceptibility measured under circumstances where the magnetic system remains in thermal equilibrium with the lattice during the measured period. This means that the thermal populations of the various crystal-field levels adjust themselves in a way according to the change in Boltzmann factors as the energies of the levels change with applied static magnetic field. The isolated susceptibility is that measured when the thermal populations of the levels do not change. The effect measured is due to the change in wavefunctions, and hence the moments, with the applied magnetic field, i.e. the polarization effect.) In case of the singlet-ground-state system, Eq. (4) signifies that the population fluctuation in the excited crystal-field states of the host magnetic ions contributes to the line broadening of the $Gd^{3+}$ probe. This means that we expect the linewidth of $Gd^{3+}$ in a singlet-ground-state system to increase sharply as the temperature is raised to the order of the crystal-field splitting to the first excited state of the host magnetic ions: and if the temperature is high compared to the overall crystal-field-splitting, we expect the linewidth to be temperature independent. Since the isothermal and isolated susceptibilities are directly related to the crystal-field splittings, the measurements of the EPR linewidth of $Gd^{3+}$ can provide very useful information about the crystal-field splittings of the host non-Kramers ions. As demonstrated in Refs. 12 and 13 the crystal-field splittings in Tm and Pr monopnictides agree with those obtained by neutron scattering. However, if the ground-state of the host magnetic ion is magnetic, the $Gd^{3+}$ probe linewidth is expected to be very broad and nearly temperature-independent. Therefore, by studying the temperature dependence of the $Gd^{3+}$ probe linewidth we may determine whether the ground-state of the host magnetic ion is magnetic or not. Therefore, this technique can be used to identify the valence state of the host magnetic ions.

## C. Motional Narrowing

Motional narrowing was first discussed in the classic paper[21] by Bloembergen, Purcell, and Pound (BPP). Anderson's explanation[22] of the phenomenon will be presented here. It is clear that non-magnetic interactions cannot affect the magnetic resonance line directly. The magnetic interactions responsible for the linewidth depend on the positions of the magnetic ions. Some non-magnetic interactions cause the actual random motions of the ions, and the magnetic interactions will then vary in time in some way controlled by the ionic motions. As a result, the magnetic resonance line experiences a time averaged-effect of the magnetic interactions. When the ionic motions are sufficiently rapid, this average effect may be much smaller than otherwise. Therefore the broadening effect of the magnetic interactions is reduced; the resonance line is narrowed and this is called motional narrowing.

Actually, before BPP, the phenomenon of exchange narrowing was discussed by Gorter and Van Vleck.[23,24] Since the mechanism is in principle the same in both motional and exchange narrowing, we will first discuss the phenomenon of exchange narrowing in $CuSO_4 \cdot 5H_2O$, and then apply this result to our case. In $CuSO_4 \cdot 5H_2O$, there are two inequivalent $Cu^{2+}$ sites in a unit cell. Consequently, there are two g-values, $g_1$ and $g_2$, and two corresponding resonance absorption lines. This spectrum was observed[25] at 30 GHz. However, when the microwave frequency was lowered to 10 GHz, only one narrow line was observed.[25] This phenomena may be explained in the following classical language.

Since $J/h$ where $J$ is the exchange interaction coefficient between the spins on sites 1 and 2, may be taken to be the rate at which the resonant spin on sites 1 and 2 "exchange", the spins precess at frequency $g_1 \beta H_o/h$ for a while and then at $g_2 \beta H_o/h$. If the rate at which the exchange between these two Larmor frequencies is faster than $|g_2 - g_1| \beta H_o/h$, then the line is "exchange narrowed". A theoretical model calculation appropriate to this problem has been made by Anderson.[22]

The situation for TmSe is similar to this example. In TmSe, Tm fluctuates between $Tm^{2+}$ and $Tm^{3+}$ at the rate of $\sim 10^{11}$ per sec.[2] If $g_1$ and $g_2$ are the g-values of the $Gd^{3+}$ impurity probe when all the surrounding Tm are $Tm^{2+}$ and $Tm^{3+}$, respectively, the fluctuating Tm ions will cause the $Gd^{3+}$ g-value to fluctuate between $g_1$ and $g_2$ at the rate ($\sim 10^{11}$ per sec.) much faster than $|g_2 - g_1| \beta H_o/h$. In this case, the line is "motionally narrowed" by the valence fluctuations, and a single narrow line is expected.

## EXPERIMENTAL RESULTS

The powder samples[14] of TmS, TmTe, and TmSe doped with $Gd^{3+}$ were used in this investigation. They were prepared by a method similar to that described in Refs. 12 and 13. All these samples have the cubic NaCl structure,[3] and hence the g-values are isotropic. The EPR spectometer used is a conventional one operating at 9.2 GHz.

## A. TmS

Fig. 1(a) displays the temperature dependence on the Gd$^{3+}$ EPR linewidth of 0.1 at. % GdS in TmS. The linewidth increases with temperature. Following our theoretical discussion in the last section, this temperature dependence suggests that the Tm ions in TmS are trivalent with non-magnetic ground-states. This conclusion is in agreement with the energy level scheme of Tm$^{3+}$ in TmS assumed by Bucher, et al.[3] For Tm monopnictides,[10,12,13] x ≈ -1, where x is

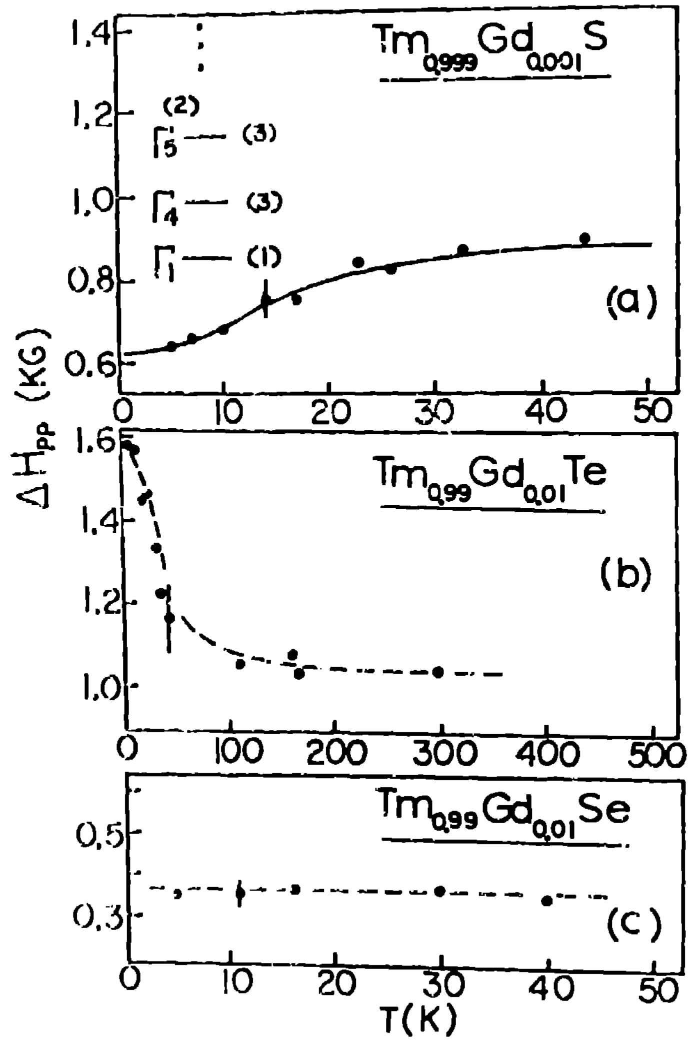

Fig. 1. Gd$^{3+}$ EPR linewidth versus temperature for (a) 0.1 at. % GdS in TmS, (b) 1 at. % GdTe in TmTe, and (c) 1 at. % GdSe in TmSe.

the crystal-field parameter as defined by Lea, Leask, and Wolf.[26] If we also assume x = -1 for TmS, the crystal-field level scheme of Tm$^{3+}$ is as depicted in the inset of Fig. 1(a), and TmS is a singlet-ground-state system. By fitting Eq. (4) with the wavefunctions provided in Ref. 26 to the data, we obtain the solid curve in Fig. 1(a) with the crystal field splitting $E(\Gamma_4) - E(\Gamma_1) = 15 \pm 3$ K. This value of the splitting is in close agreement with that (16 K) estimated by Bucher, et al.[3] from their specific heat data. It is interesting to note that there is no linewidth anomaly near the Néel temperature[3] of TmS (5.18 K) due to the critical slowing-down as is predicted and observed in the pure antiferromagnet.[27] The absence of this anomaly is attributed[28] to the weak exchange interaction between Gd$^{3+}$ and Tm$^{3+}$.

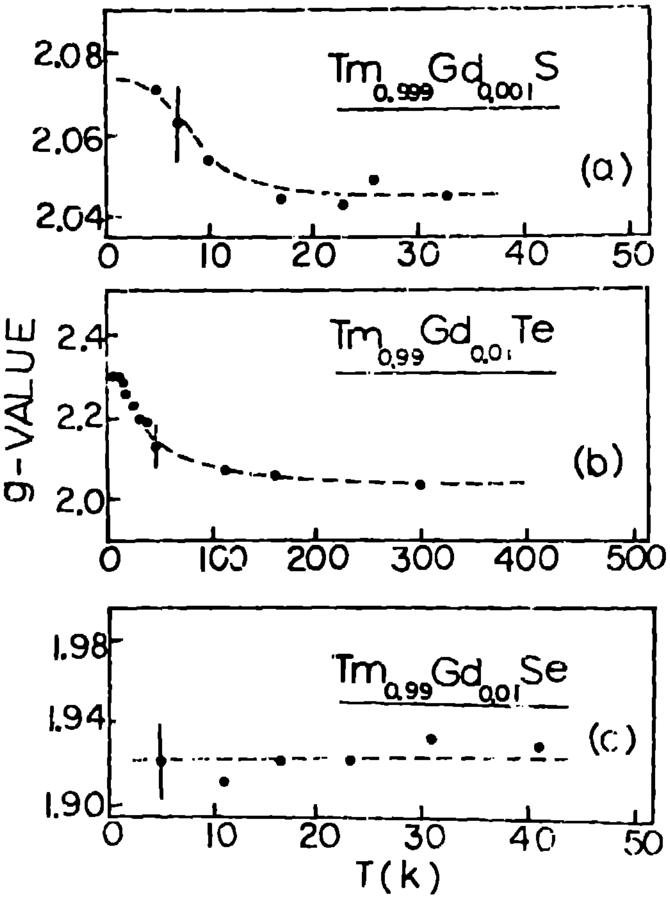

Fig. 2. Gd$^{3+}$ resonance g-value versus temperature for (a) 0.1 at. % GdS in TmS, (b) 1 at. % GdTe in TmTe, and (c) 1 at. % GdSe in TmSe.

Fig. 2(a) depicts the temperature dependence of the $Gd^{3+}$ g-value. The temperature dependent part of the g-value is similar to those of other singlet-ground-state systems.[12,13] Accordingly, the data of the g-measurement also support the idea that Tm in TmS is trivalent. Using Eq. (2), we obtain the exchange interaction coefficient $J(0) = +0.74 \pm 0.07$ K, in which the positive sign denotes that $Gd^{3+}$ and $Tm^{3+}$ are ferromagnetically coupled.

## B. TmTe

First, let us examine the consequences of the assumption that Tm in TmTe is divalent. According to Lea, Leask, and Wolf,[26] the ground-state is the $\Gamma_6$ doublet and the excited states are the $\Gamma_7$ doublets and the $\Gamma_8$ quartet. Since the $\Gamma_6$ ground-state is magnetic, and by using Eq. (4) and the wavefunctions provided by Lea, Leask, and Wolf,[25] the linewidth of the $Gd^{3+}$ probe in TmTe is expected to increase slightly with increasing temperature. Contrarily, as shown in Fig. 1(b), the data of 1 at. % GdTe in TmTe demonstrate that the $Gd^{3+}$ linewidth decreases drastically from 5 K to 40 K. This surprising temperature dependence is believed to originate from the presence of the "extra" electrons contributed by the doping of the <u>trivalent</u> Gd ions into a host of the <u>divalent</u> Tm ions as required by charge compensation. In analogy to the case[16] of $Gd^{3+}$ in $Sm^{2+}$ monochalcogenides, we assume that there is an "extra" electron localized around the $Gd^{3+}$ ion in a cubically symmetrical orbital. The presence of the "extra" electron contributes directly to the exchange interaction between the $Gd^{3+}$ ion and its surrounding Tm ions. This "extra" exchange interaction in turn contributes to the line broadening. At high temperatures, the "extra" electron is delocalized, resulting in the reduction of the $Gd^{3+}$ - $Tm^{2+}$ exchange interaction and, hence, giving rise to the decrease of the $Gd^{3+}$ probe linewidth. From the temperature dependence of the linewidth the activation energy needed to delocalize the "extra" electron has been estimated to be ∿ 50 K.

According to Eq. (2) the temperature variation of the exchange interaction should be also reflected in that of the g-value. As shown in Fig. 2(b), the g-value also decreases with increasing temperature. Utilizing Eq. (2), $J(0) = 1.3 \pm 0.1$ K at $T = 5$ K.

Walsh, et al.[29] pointed out that the higher concentration of $Gd^{3+}$ in Sm monochalcogenides could result in the delocalization of the "extra" electrons and the decrease of the g-shift. For this reason we have investigated 3 at. % GdTe in TmTe. As expected, the g-shift observed has been found to be much smaller than that of the 1 at. % samples. In addition, the linewidth of our 3 at. % samples is nearly temperature independent, indicating that the ground-state of $Tm^{2+}$ is magnetic. In order to further support the idea of "extra" electrons, we have measured the electrical conductivity It is known that pure TmTe is a semiconductor.[3] However, all our Gd doped samples exhibit that the electrical conductivity decreases with increasing temperature, and hence they are metals. This observation suggests that Gd are donors, and when the Gd concentration is high enough, the sample becomes metallic.

### C. TmSe

The interconfigurational fluctuations of a Tm ion arises from an interplay of conduction electrons with the unstable 4f shell of the Tm ion.[30] Accordingly, we expect the exchange interactions between a $Gd^{3+}$ probe and its neighboring Tm ions, $J$, to fluctuate in addition to the valence fluctuations of Tm. Even though the detailed nature of the exchange interactions is not known, we would anticipate that $J$ fluctuates, more or less, at the same rate as that of the valence fluctuation of Tm. Consequently, in computing the linewidth following the theory of Moriya and Obata,[19] we should first calculate the time auto-correlation function of the form:

$$\langle J(t)\ S_j(t)\ J(0)\ S_j\ (0)\rangle,$$

where $J(t)$ is the exchange interaction coefficient between the $Gd^{3+}$ ion and its j-th neighboring Tm ion at time t. At present, there is no computed result of this joint auto-correlation function including the fluctuations of both $J$ and $S_j$. However, according to the Mössbauer data,[2] the valence of Tm and hence $S_j$ fluctuates at the rate[31] of $\sim 10^{11}$ $sec^{-1}$, which is somewhat greater than our microwave frequency ($9.2 \times 10^9$ $sec^{-1}$). Hence, it is reasonable to assume that the correlation time of the joint time auto-correlation function to be $\tau_c \lesssim 10^{-11}$ sec. In the paramagnetic regime, if the temperature is not very close to the critical temperature, according to our data presented above and those in Refs. 12, 16, and 18, the exchange g-shift is $\lesssim 0.4\ g_o$. Thus, at our microwave frequency (9.2 GHz), the separation between a $Gd^{3+}$ line due to the influence of $Tm^{2+}$ and that due to $Tm^{3+}$, $|g_2 - g_1|\beta H_o/h$, is on the order of $10^9$ $sec^{-1}$. This separation is much less than the fluctuation rate of $\sim 10^{11}$ $sec^{-1}$. In this extreme "motional narrowing" case, based on our discussion presented in the last section, the resonance absorption is expected to be a narrow line. This is exactly what was observed. Fig. 1(c) shows the linewidth data for 1 at. % GdSe in TmSe. The linewidth is temperature independent within our experimental accuracy and is only ∿ 350 Gauss. This narrow linewidth is believed to be partly due to the zero-field splitting of the S-state $Gd^{3+}$ ($S = 7/2$) and partly due to the $Gd^{3+}$ - $Gd^{3+}$ dipole interactions. Fig. 2(c) depicts our g-value data from 5 K to 40 K. Within our experimental errors, the g-value is independent of temperature, and is 1.92 ± 0.02. This g-value yields that the g-shift, $\Delta g = -0.07$, where the minus sign indicates that the Gd$^{3+}$ probe is "coupled" to the neighboring Tm ions antiferromagnetically.

## CONCLUDING REMARKS

It is evident that the application of the Gd$^{3+}$ probe EPR technique to the study of mixed-valence systems is still at an early stage and much more work has to be done in order to understand the physics associated with the technique with confidence. Several problems of interest are: (1) The theory of the fluctuating exchange interaction, $\mathcal{J}(t)$, between Gd$^{3+}$ and the fluctuating host magnetic ion. (2) The theory of the joint auto-correlation function including $\mathcal{J}(t)$ and $S_i(t)$. (3) The theory of the zero-field splitting of Gd$^{3+}$ in a valence-fluctuating host. (4) The theory of the Gd$^{3+}$ probe lineshape and linewidth, including the effects of conduction electrons.

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