

Electrical resistivities of liquid K-Sn and Cs-Sn alloys and the liquidus of the K-Sn system

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The electrical resistivity ρ of liquid K-Sn and Cs-Sn alloys has been measured as a function of composition and temperature. The resistivities of both systems exhibit very sharp peaks close to the equiatomic composition. At the same composition, the temperature dependence of the resistivity has a deep minimum. The maximum resistivities are 3100 and 14 200 $\mu\Omega$ cm, respectively. A comparison with the Li-Sn and Na-Sn alloys and with the alkali-lead systems strongly suggests that Zintl ions are formed in the liquid. Finally the liquidus curve of the K-Sn system was determined resistometrically.

I. INTRODUCTION

Polyanion formation in liquid ionic alloys has been intensively studied during the last decade. A classical example is formed by the alkali-lead alloys in which equiatomic liquid compounds occur, characterized by the formation of so-called Zintl ions. In this case, the Zintl ions are tetrahedral units $(\text{Pb}_4)^{4-}$, which are isoelectronic to As_4 . For reviews the reader is referred to Refs. 1–3.

Evidence for the existence of compounds in the liquid state is often obtained by studying the behavior of suitable physical properties, like electrical resistivities,^{4–6} Knight shifts,⁷ and thermodynamic properties,^{8,9} as a function of composition. Distinct maxima or minima then define the “stoichiometric composition.” Strong evidence has also been obtained from numerous neutron-diffraction experiments.^{10–12}

According to a rule due to Geertsma,¹³ this kind of polyanion formation is essentially a size effect: with increasing diameter of the alkali atom, the Zintl ion becomes more stable. In Li-Pb, a simple octet compound Li_4Pb is formed, whereas in the systems K-Pb, Rb-Pb, and Cs-Pb equiatomic compounds with Zintl ions are found. Another result from Geertsma’s work is that also the electrical resistivities increase strongly with increasing size of the alkali metal, in complete agreement with experiments.

From previous studies (resistivity,¹⁴ thermodynamic properties,¹⁵ neutron diffraction,¹⁶ and Knight shift^{7,17}), it is expected that there exists a strong similarity between the alkali-tin alloys and the alkali-lead alloys. Until recently, experimental difficulties prohibited us from performing measurements of the electronic properties of K-Sn, Rb-Sn, and Cs-Sn, which are most likely to exhibit polyanion formation. We have succeeded now in carrying out measurements of the electrical resistivity for the whole composition range of K-Sn and for the most important range of the Cs-Sn system.

The hypothesis of Zintl-ion formation in the liquid alloys is partly based on analogies with the crystal structure. All the solid equiatomic compounds NaPb, KPb, RbPb, CsPb, NaSn, KSn, and RbSn are isomorphic with

space group $I4_1/acd (D_{4h}^{20})$,^{10,18–21} contain tetrahedral Zintl ions as structural units and are congruently melting (at least those of which the phase diagrams are known). A drawing of the unit cell can be found in Refs. 3 and 22. Very conspicuous are the tetrahedral Pb_4 or Sn_4 units. It is interesting then that, in Cs-Sn, the crystalline Zintl phase is unstable at high temperatures and the congruently melting compound has shifted from 50 to 60 at. % Sn.²¹ For K-Sn, no complete phase diagram could be found in the literature. We have determined the liquidus resistometrically in the course of the investigation.

II. EXPERIMENT

Potassium with a nominal purity of at least 99.99 wt. % was supplied by Kawecky Beryllco Industries, and cesium having a purity of 99.999 wt. % was obtained from Ventron GmbH. Tin shots, purchased from Ventron GmbH, had a nominal purity of 99.999 wt. %. All the samples were prepared inside a He-filled glove box with oxygen content lower than 1 ppm. The resistivity measurements were carried out in the same glove box.

For the K-Sn system, the metal tube method was used. The experimental setup was essentially the same as used previously for the liquid alkali-Bi (Ref. 23) and Li-Ge (Ref. 24) systems. After performing corrosion tests, we decided to use molybdenum tubes for the larger part of the composition range. For K-rich alloys, AISI 321 stainless steel, which is much easier to handle than molybdenum, could be used because no significant corrosion by K-Sn occurs up to 700 °C as long as the Sn content is less than 35 at. %. A description of the construction of the molybdenum tube can be found in a recent paper.²⁵ Since the vapor pressures are very high indeed in the liquid K-rich alloys, in some cases we used the technique of closing the top of the measuring tube by a plug of solidified alloy. It was checked that no significant temperature gradient developed in the tube section used for the measurements.

Since the relative error of measurements with the metal tube method increases with the value of resistivity of the

liquid, and the Cs-Sn system turned out to have systematically higher resistivities than the K-Sn system, the metal tube method is less favorable for liquid Cs-Sn. Therefore, a four-probe method was used for liquid Cs-Sn alloys. The setup as described by Meijer⁴ was adopted, but in order to improve the temperature homogeneity, a copper cylinder instead of a stainless-steel cylinder was mounted around the alumina measuring cell. A four-bore alumina tube with molybdenum electrodes and a shielded chromel-alumel thermocouple were dipped into the measuring liquid. The temperature stability was better than $\pm 5^\circ\text{C}$. The inaccuracy in the values for the resistivities is estimated to be $\pm 2\%$ for K-Sn and $\pm 5\%$ for Cs-Sn, respectively.

III. RESULTS

Figure 1 shows the resistivity ρ of liquid K-Sn alloys as a function of composition and for temperatures indicated in the figure. The resistivity exhibits a sharp peak at the equiatomic composition KSn, where it attains a value of approximately $3100 \mu\Omega \text{ cm}$ at 850°C . In Fig. 2, $d \ln \rho / dT$ is plotted; there is a deep, negative, minimum at 50 at. % Sn. The maximum value of $(-1/\rho)d\rho/dT$ is $9.55 \times 10^{-3} \text{ K}^{-1}$ at 850°C .

The resistivity results for the Cs-Sn alloys are shown in Fig. 3. Because of experimental difficulties (mainly eva-

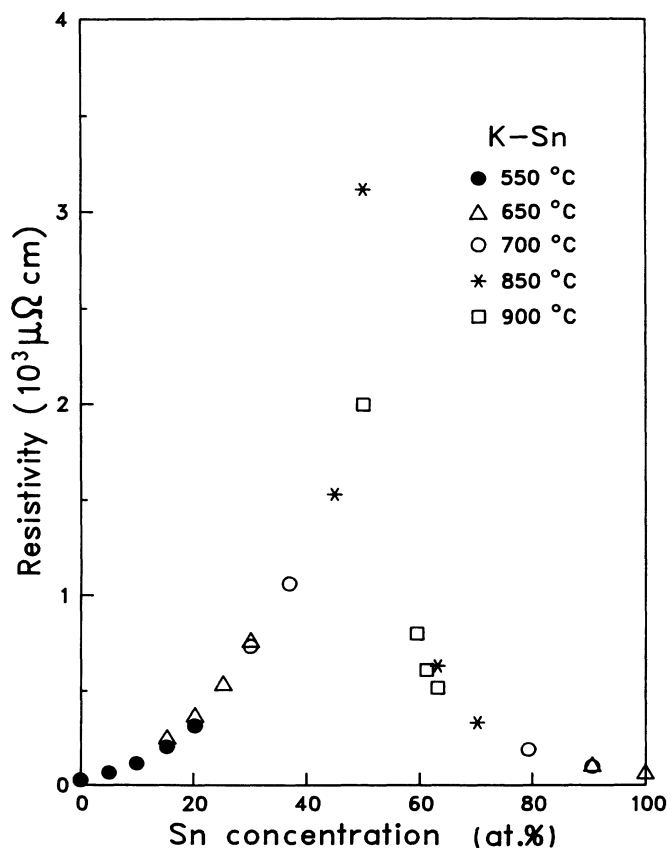


FIG. 1. The resistivity ρ of liquid K-Sn alloys as a function of composition at the temperatures indicated in the figure.

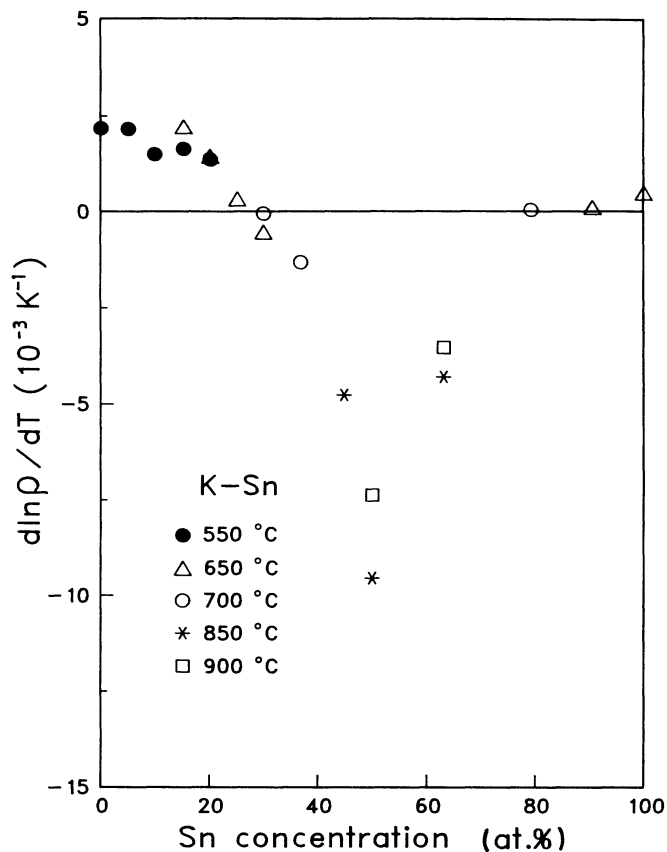


FIG. 2. The temperature dependence of the resistivity $d \ln \rho / dT$ of liquid K-Sn alloys as a function of composition at the temperatures indicated in the figure.

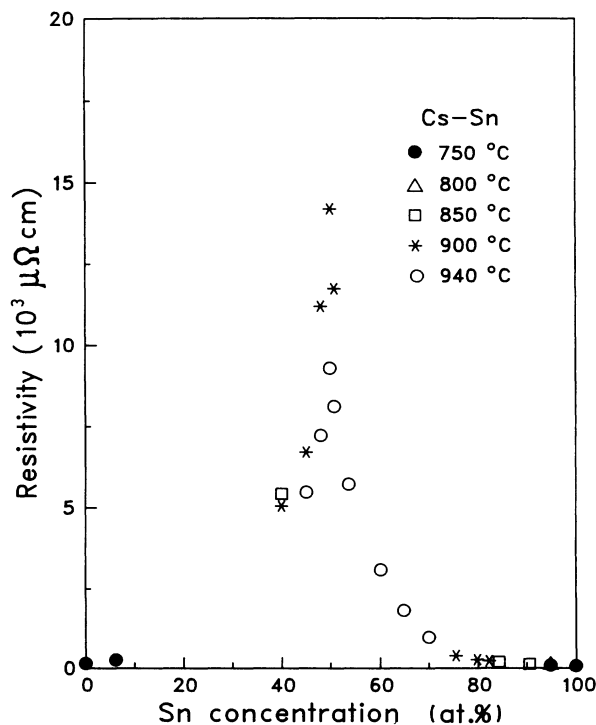


FIG. 3. The resistivity ρ of liquid Cs-Sn alloys as a function of composition at the temperatures indicated in the figure.

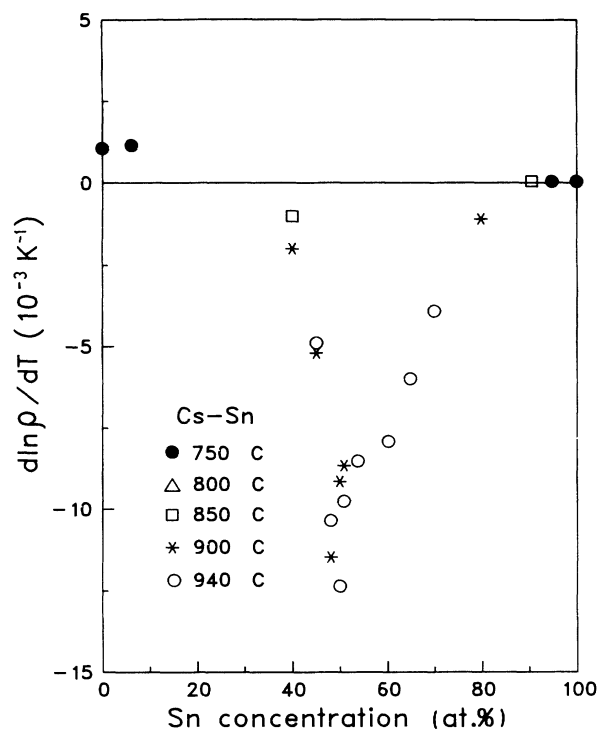


FIG. 4. The temperature dependence of the resistivity $d \ln \rho / dT$ of liquid Cs-Sn alloys as a function of composition at the temperatures indicated in the figure.

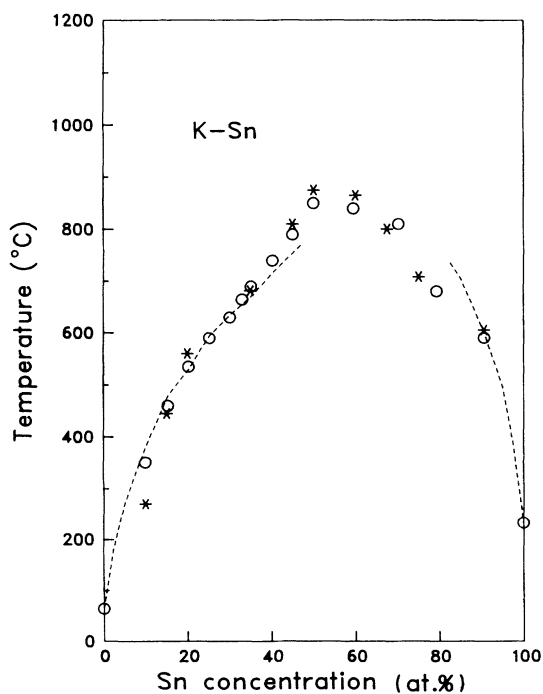


FIG. 5. The liquidus of the K-Sn system. (\circ), present work; (*), Takeda *et al.* (Ref. 26); (---), Massalski *et al.* (Ref. 21).

poration), the resistivity measurements were not successful in the alkali-rich range between 7 and 40 at. % Sn. At the equiatomic composition, the resistivity exhibits a peak which is even significantly sharper and higher than for K-Sn. It attains a value of $\rho = 14\,200 \mu\Omega \text{ cm}$ for $T = 900^\circ\text{C}$, well in the semiconducting range. The logarithmic derivative of the resistivity $d \ln \rho / dT$ is shown in Fig. 4. It has a deep, negative, minimum with a value of $-12.5 \times 10^{-3} \text{ K}^{-1}$ at 50 at. % Sn.

Finally, our results for the liquidus are shown in Fig. 5. The accuracy of the temperatures given is approximately $\pm 5^\circ\text{C}$. With a few exceptions, our results are only slightly different from those determined earlier from susceptibility measurements,²⁶ but in some composition ranges there is a larger discrepancy with the provisional results given in the phase diagram published by Massalski *et al.*²¹

IV. DISCUSSION

The measurements presented complete our experimental investigation of the electrical resistivities of liquid alkali-tin alloys (see Ref. 14 for Li-Sn and Na-Sn). Indeed, no results have been obtained for Rb-Sn, but we may safely assume that its behavior is intermediate between those of K-Sn and Cs-Sn.

The resistivity results for the liquid alkali-tin systems are summarized in Fig. 6. Note that this figure is a schematic one only: the curves are not isotherms but rather follow the liquidus at some small distance.

Obviously liquid Li-Sn forms an octet compound. On the other hand, K-Sn forms an equiatomic compound which, in our interpretation, should be considered as a Zintl compound $\text{K}^+_4(\text{Sn}_4)^{4-}$, where $(\text{Sn}_4)^{4-}$ is a tetrahedral unit. The Cs-Sn system obviously also has a sharply defined equiatomic compound. As mentioned in the Introduction, it does not correspond to a congruently melting solid compound, but we conjecture that it is a liquid Zintl compound, $\text{Cs}^+_4(\text{Sn}_4)^{4-}$, as well. In Na-Sn apparently both the octet compound and the Zintl compound have some stability and occur simultaneously.¹⁴

The existence of equiatomic compounds in K-Sn and Cs-Sn is corroborated by the experimental observation (a very qualitative one, indeed) that, in the composition range between the pure alkali metal and KSn or CsSn, strong evaporation occurs. This is an indication that the solution has a tendency to instability. In Cs-Sn, the evaporation is so strong that measurements in the composition range between 7 and 40 at. % Sn were unfeasible. The phase diagram exhibits a liquid immiscibility region for cesium-rich compositions up to 39 at. % Sn.²¹ In K-Sn as well as Cs-Sn we may compare the alkali-rich mixtures with metal-salt solutions which are known to have a low stability.²⁷

The resistivity results bear a great resemblance to those of the alkali-lead systems (see Fig. 7). Li-Pb and Na-Pb have octet compounds, but in the resistivity data for Na-Pb a weak shoulder is visible at approximately 43 at. % Pb, while in Na-Sn a high peak has developed at the corresponding composition.¹⁴ Furthermore, the K and Cs alloys with Sn have systematically higher resistivity maxi-

ma than those with Pb. This is all in excellent agreement with Geertsma's model,¹³ which is described in terms of transfer integrals U and V between Pb or Sn atoms. U is the intracluster integral and V the intercluster integral. When U increases or when V decreases, the stability of the configuration containing tetrahedral clusters is increased relative to the nonclustered configuration. Keeping the anion equal, V decreases strongly from Li to Cs because Cs is much larger than Li and the Cs ions force the clusters to be further apart. For example, the smallest distance between Pb atoms on different tetrahedra is 3.668 Å in crystalline NaPb and 4.691 Å in CsPb.¹⁰ This is the cause of the octet-clustered transition which, in the lead alloys, takes place between Na-Pb and K-Pb. It is also the cause of the rapid increase of the maximum resistivity from K-Pb to Cs-Pb (respectively, K-Sn to Cs-Sn), as the electrical conductivity is mainly determined by electron hopping from one tetrahedron to the other.

Now U is larger for Sn than for Pb (stronger covalent interaction). This is reflected in the intratetrahedron distances: e.g., in NaSn the shortest Sn-Sn distance is 2.967 Å,¹⁹ while the Pb-Pb distance in NaPb is 3.158 Å.¹⁰ Consequently, for the Sn alloys, the onset of clustering in the sequence Li, Na, K, Rb, Cs will be shifted somewhat in the direction of the smaller alkali atoms. Comparing the results for Na-Pb and Na-Sn, we see that this is exactly what has been found experimentally. Some relevant crystallographic data have been collected in Table I.

TABLE I. Shortest interatomic distance (given in Å) in crystalline alkali-Sn, Pb alloys. (The intercluster distance is the shortest distance between two Sn or Pb atoms on different tetrahedra.)

		Sn-Sn	Pb-Pb
Na	Intracluster	2.967 ^a	3.158 ^c
	Intercluster	3.760 ^a	3.668 ^c
K	Intracluster	2.980 ^b	3.113 ^c
	Intercluster	4.330 ^b	4.164 ^c
Cs	Intracluster		3.074 ^c
	Intercluster		4.691 ^c

^aReference 19.

^bReference 18.

^cReference 10.

The Fermi energy E_F is in the covalent (pseudo)gap deriving from the tetrahedral units.²² The density of states at E_F is likely to be higher in the Pb alloys than in the Sn alloys and, consequently, the resistivities are systematically lower in the lead alloys than in the Sn alloys.

The apparent success of Geertsma's model needs some qualification. We have tacitly assumed that at the equiatomic composition all the Sn atoms participate in the

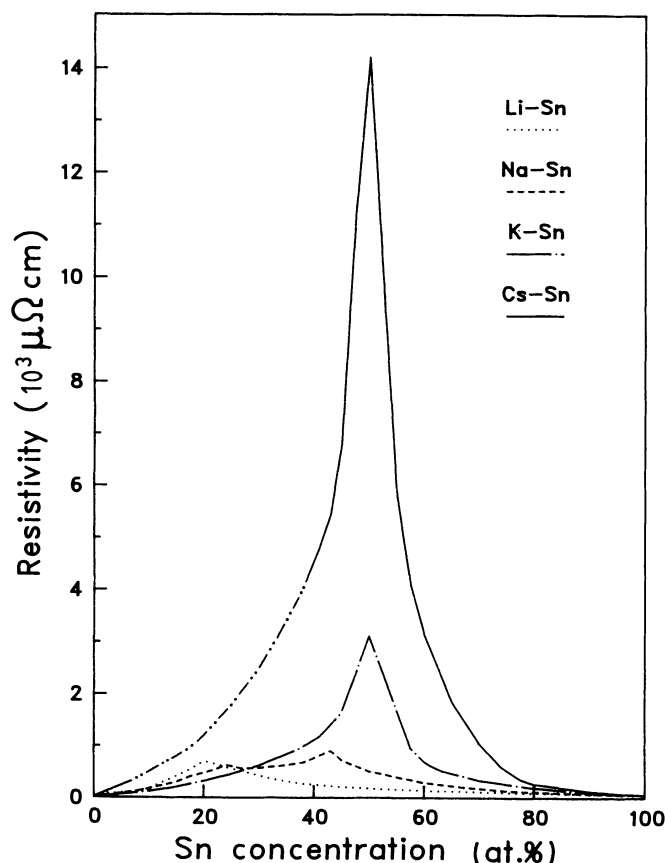


FIG. 6. The resistivities ρ of liquid alkali-Sn alloys near the liquidus temperature.

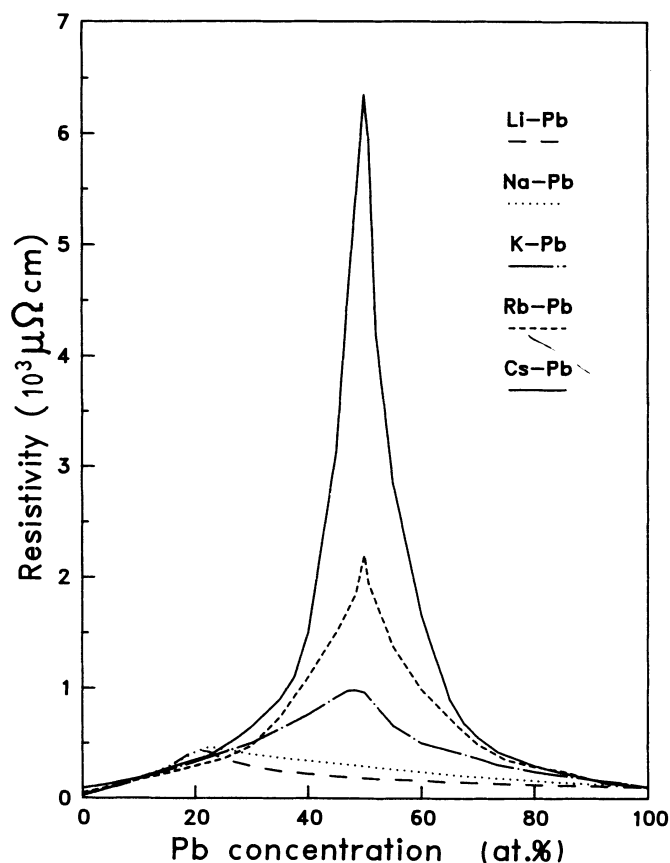


FIG. 7. The resistivities ρ of liquid alkali-Pb alloys near the liquidus temperature.

tetrahedra. The large, negative, $d\rho/dT$ as well as thermodynamic investigations⁹ indicate that this cannot be true and that dissociation takes place, most probably already at the melting point. The thermodynamic consequences are discussed in Ref. 9, but the effect on the resistivities is still not clearly understood.

Recently, accurate neutron-diffraction experiments have been performed on liquid equiatomic KSn and CsSn.¹⁶ The results are in excellent agreement with the polyanion picture. The intracluster Sn-Sn distance in the liquid proves to be significantly shorter than the corresponding Pb-Pb distance and comes close to the distance found in the crystal. From the decrease of the superstructure peak with temperature, it is concluded that dissociation must indeed occur. In general, evidence was found for the tendency to clustering being stronger in the alkali-Sn alloys than in the alkali-Pb alloys. There is good agreement with analytical model calculations in-

volving long-lived neutral $A_4(\text{Sn}_4)$ units.¹⁶

Concluding, we may say that the liquid alkali-lead and alkali-tin alloys behave very similarly, and can be described from one single point of view, essentially the model proposed by Geertsma.

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