Transition to Semiconducting Characteristics in Liquid Alkalimetal-Antimony-Alloys

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The paper reports new measurements of the electrical conductivity, thermoelectric power, magnetic susceptibility, and molar volume of liquid Cs-Sb alloys and, partly, Na-Sb and K-Sb alloys. From the temperature and composition dependence of the electronic properties it is concluded that typical semiconducting behavior similar to liquid chalgogen based alloy semiconductors exists over a wide composition range. The change in bonding for $0.25 \leqq X_{\mathrm{Sb}} \leqq 0.5$ is qualitatively discussed and it is found that these liquid alloys are not essentially ionic in character.

Introduction

Among the group of liquid alloy semiconductors two main types are currently distinguished: those which are based on the chalcogens and those in which both components, in the pure liquid state, are metallic in character but which change to nonmetallic states near some stoichiometric compositions – for recent reviews see [1–4]. A common feature of such liquid alloys is that for some concentration and temperature range the electronic properties are similar to semiconductors although a distinction from other liquids such as molten salts or molecular liquids is rather complex. This directly reflects the problem of the nature of chemical bonding in connection with the discussion of the electronic structure in these liquids which is of much current interest. In the limit of large charge transfer between the electropositive and electronegative element – like in CsAu – an ionic description seems to be appropriate [4–9]. On the other hand, the structural properties of some liquid metal-chalcogen alloys like Ag_2Te are consistent with a molecular model, i. e. the valence requirements may be satisfied within a molecule – see e. g. [1–3].

In the case of metal-metal alloys the existing structural informations, see e. g. [3, 10], led Enderby to the suggestion that "*all* these systems should be essentially ionic in character". In general, however, one may envisage a combination of elements where the electronegativity difference is not very large and where the electronic configuration of one component approaches e. g. that of a chalcogenide element. In this respect a continuous variation between the extreme limits of an ionic and molecular model should be possible and should be taken into account for the group of metal-metal alloys itself.

We think that the alkalimetal-antimony alloys represent an example of this type. The results which we report here are in support of this view. In the solid state these elements form well-known compound semiconductors with various stoichiometries ranging from A_3Sb to ASb (A = alkalimetal) – see e. g. [11, 12]. The phase diagrams are characterized by well defined maxima of the liquidus curve at these compositions and give indications for further compounds stable at different temperatures in the range of $0.25 < X_{\mathrm{Sb}} \leqq 0.70$, see e. g. [13, 14]. The melting points of the highest melting compounds are: 725 °C (Cs_3Sb), 812 °C (K_3Sb), 856 °C (Na_3Sb).

We have continued our previous study of the Cs-Sb system [15] for higher antimony concentrations and report new results of the electrical transport properties, the magnetic susceptibility, and the molar volume including new measurements of liquid Na-Sb and K-Sb alloys.

Experimental Details

In the present measurements on liquid alkalimetal-antimony alloys special care had to be taken of the problems of chemical reactivity at high temperatures and tight sealing of the liquid containers. Molybdenum, niobium, and alumina of high purity proved to be chemically stable in contact with the alloys up to 900 °C. This was controlled by the reproducibility of the measurements on different heating and cooling cycles and by inspection of the surface quality of

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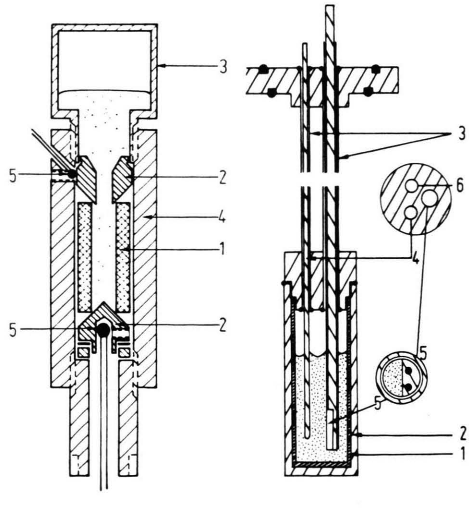
these materials after they had been in contact with the alloys at high temperature. Visible attack of molybdenum and niobium by antimony was noticed at temperatures above 1000 to 1100 °C. Sealing of the liquid containers was achieved by mechanical squeezing of specially formed niobium parts. Details of the different cell constructions are described below. All sample preparations were performed under purified argon atmosphere inside a glove box. Starting materials for alloy preparation were of 99.95% total purity (alkali metals, alfa products) and 99.999% metal purity (antimony, alfa products).

1. Electrical Transport Measurements

The cell constructions for the measurements of the electrical conductivity and the absolute thermoelectric power (Seebeck coefficient) are shown schematically in Figure 1. Two types of construction with different electrode arrangement and liquid container have been used. In type (a) the liquid compartment for resistance measurement is defined by an alumina tubing (1) – length = 35 mm, inner diameter = 3.2 mm – which is mechanically sealed by niobium cone fittings (2) and is connected with a liquid reservoir from molybdenum (3) as drawn in Figure 1 a. The niobium parts are fixed and strongly squeezed inside a molybdenum tubing (4) whereby the lower niobium cone is electrically insulated via an alumina disc. The tips of two Pt/Pt-13Rh thermocouples (5) are screwed on the niobium cones. These are used both for temperature control and as electrodes for resistance measurement which has been performed with a conventional four probe method using both ac and dc techniques. For the conductivity determination the cell constant was calculated from the dimensions of the alumina tubing. In each conductivity experiment ohmic characteristics have been checked. The cell was surrounded by two separate resistance heaters mounted inside a vacuum vessel. For thermopower measurement different temperature gradients ΔT up to a maximum of 5 deg/cm have been applied. The corresponding voltage differences ΔV have been measured via the Pt-legs of the thermocouples and the thermoelectric power was determined from the slope of ΔV vs. ΔT-plots and corrected for the Pt-contribution.



a) b)

Fig. 1. Cell constructions for electrical transport measurements. Type (a): alumina tubing (1), niobium cone fittings (2), liquid reservoir (3), molybdenum tubing (4), Pt/Pt-13Rh thermocouples (5). Type (b): molybdenum cylinder (1), stainless steel vessel (2) and refluxing capillaries (3), thermocouple capillary (4), four bore alumina conductivity cell (5), refluxing column for addition of Sb (6).

Two disadvantages of this cell construction should be mentioned. Liquid alloys were prepared by filling weight amounts (±1 mg accuracy) of the component materials into the reservoir and after reaction for several hours above the liquidus temperature of the compound with the highest melting point the measuring compartment was filled by turning the reservoir upwards. However, this procedure in many cases did not immediately yield a perfect contact between the electrodes – probably due to bad wetting by the liquid – but only after further heating and shaking of the cell reproducible conditions were reached. A second difficulty concerns the accurate control and reproducibility of the concentration of the alloys which was not better than ±0.2 at% Sb.

In particular this problem in connection with the observed steep concentration dependence of the conductivity near stoichiometric Cs_3Sb [15] made a different cell construction necessary which is drawn schematically in Figure 1 b. This device follows the technique used by Pfeifer, Heus, and Egan [16] and in principle consists of a large liquid container of about 20 cm^3 volume into which dips an alumina conductivity cell. In the construction used here the liquid is contained in a molybdenum cylinder (1) inside a stainless steel vessel (2) to which three stainless steel capillaries of about 25 cm length (3) are sealed by argon arc welding. At the upper cold

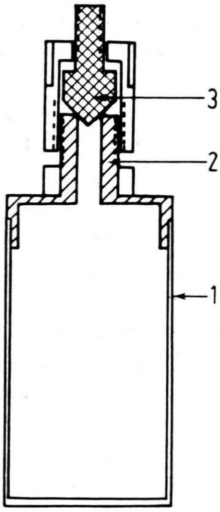


Fig. 2. Cell construction for magnetic susceptibility measurement: molybdenum cylinder (1), 50 molybdenum-50 rhenium flange (2), niobium cone fitting (3).

end these capillaries lead to a vacuum flange where the connection with a vacuum furnace is made. One capillary contains a thermocouple shielded by an alumina tubing closed one end (4), the second contains the conductivity cell (5), and the third capillary acts as a refluxing column (6) and allows adding of antimony during the experiment is running. Thus composition changes in very small steps are possible. The conductivity measuring compartment is made from a four bore alumina tubing half cut over 2 cm length at one end and surrounded by a second alumina tubing – see the cross sectional view in Figure 1 b. Molybdenum wires are used for electrodes. The cell constant for conductivity determination was calibrated with pure liquid alkali metal. All connections at the cold end have been vacuum tight and those of the conductivity tubing were flexible so that stirring of the liquid alloy was possible in order to get a homogeneous mixing in a relatively short time. During the experiment the systeem was kept under several hundred Torr argon pressure.

2. *Magnetic Susceptibility Measurement*

For the magnetic susceptibility measurement the Faraday method has been used. A typical construction of the liquid container used is shown schematically in Figure 2. It consists of a thin walled molybdenum cylinder (1) made from vacuum molten molybdenum of high purity and has the following dimensions: outside diameter = 11 mm, inside diameter = 10.6 mm, lenght = 20 mm. A flange (2) from 50 molybdenum – 50 rhenium is electron beam welded to this cylinder. Sealing is done by a niobium cone fitting (3) as sketched in Figure 2. The magnetic susceptibility of the alloys was determined from the difference of two measurements of the filled and empty cell, respectively. The cell was sealed either under vacuum or purified argon atmosphere. For further details of the apparatus and technique used see references [7, 17, 18].

3. *Density Measurement*

For the density measurements of liquid cesium-antimony alloys an apparatus designed by Kempf and Schmutzler [19] has been used. The liquid alloy is contained in a closed molybdenum tube. In principle the density of the liquid is determined from the balance of the torque of the the measuring cell. For details of this construction and the necessary evaluation procedure reference is given to the original paper [19].

Experimental Results

The results of the electrical conductivity, σ, of liquid $Na_{1-x}Sb_x$ and $Cs_{1-x}Sb_x$ are plotted in Fig. 3 versus mole fraction of antimony for different temperatures above the corresponding liquidus temperatures up to 900 °C. For the sodium system data have been obtained in two separate runs with the

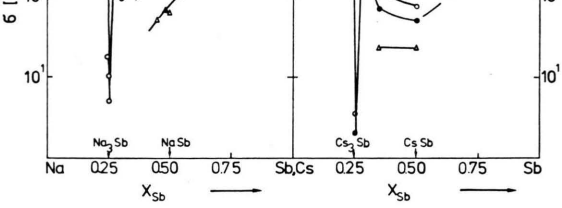


Fig. 3. Electrical conductivity, σ, of liquid $Na_{1-x}Sb_x$ and $Cs_{1-x}Sb_x$.

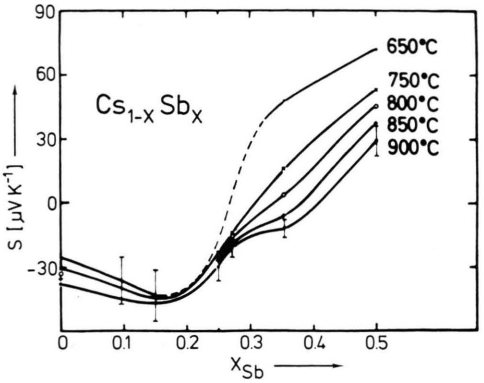


Fig. 4. Absolute thermoelectric power, S, of liquid $Cs_{1-x}Sb_x$.

conductivity cell type (b) and have been reproduced for a concentration near Na_3Sb and the compound composition NaSb with the cell type (a). In the case of the cesium system all data have been measured with the cell type (a). With exception of the concentration range near Na_3Sb and Cs_3Sb the maximum relative error is estimated to be ±30%, whereas the reproducibility of the minimum value of σ for Na_3Sb taken with the reflux cell was not better than ±80% and it is given as $5\ \Omega^{-1}\,cm^{-1}$ at 900 °C. For Cs_3Sb the minimum observed value at 800 °C is $2\ \Omega^{-1}\,cm^{-1}$ with a large absolute uncertainty corresponding to the steep concentration dependence of σ at this composition. The data of the pure alkali elements plotted in Fig. 3 have been taken from the literature [20].

The absolute thermoelectric power, S, of liquid $Cs_{1-x}Sb_x$ is represented in Fig. 4 for different temperatures up to 900 °C and concentrations up to $X_{Sb} = 0.5$. The main error contribution in these data is due to the uncertainty in ΔT. Typical error bars are indicated in Fig. 4. The values of pure cesium have been taken from [21].

In Fig. 5 the experimental results of the molar magnetic susceptibilities, χ_m, of $Na_{1-x}Sb_x$, $K_{1-x}Sb_x$, and $Cs_{1-x}Sb_x$ are summarized. The data represent the average obtained in different separate runs – different cells, different fillings – and have been reproduced e.g. for liquid Na_3Sb in three different experiments to better than $\pm 1 \cdot 10^{-6}$ emu g-atom^{-1}. The maximum absolute error of the results is estimated to be $\pm 2 \cdot 10^{-6}$ emu g-atom^{-1}. Thus a disagreement remains between our value of $-17 \cdot 10^{-6}$ emu g-atom^{-1} for Na_3Sb at 900 °C and that reported by Hackstein et al. [22] of $\approx -25 \cdot 10^{-6}$ emu g-atom^{-1}. As for the susceptibility of pure potassium it has to be noticed that here the reproducibility was not satisfactory and that deviations between different fillings of about 10% have been observed. This may be due to oxygen impurities, a problem which has been pointed out before by Flynn and Rigert [23].

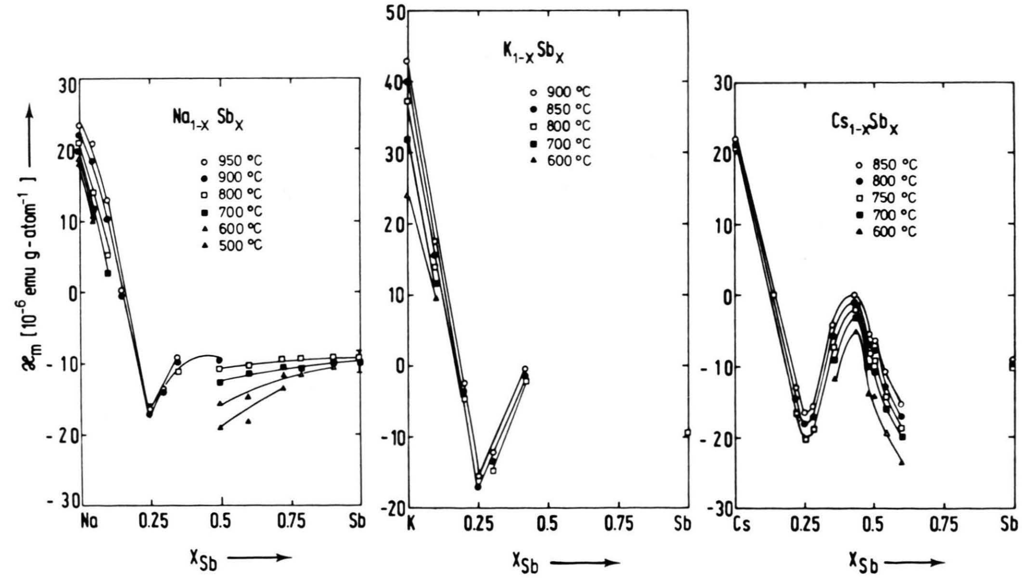


Fig. 5. Molar magnetic susceptibility, χ_m, of liquid $A_{1-x}Sb_x$-alloys (A = Na, K, Cs).

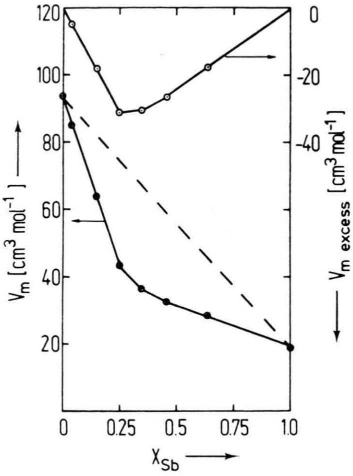


Fig. 6. Molar volume, V_m, — left scale — and molar excess volume — right scale — of liquid $Cs_{1-x}Sb_x$ at 800 °C.

The molar volume, V_m, together with the molar excess volume of liquid $Cs_{1-x}Sb_x$ at 800 °C is given in Figure 6. The error analysis of these data follows the discussion of [19] and the maximum error relative to the molar volume of pure cesium [20] which has been used for calibration is estimated to be ± 2%.

Discussion

For a rough classification of the liquid phase region into metallic and nonmetallic states a consideration of the magnitude of the electrical conductivity σ gives a first rather direct survey. In the current discussion of metal-nonmetal (M-NM) transitions in disordered systems three transport regimes are distinguished in general — see e. g. [1, 24 – 26]:

i) metallic transport should prevail if $\sigma \gtrsim 2000\ \Omega^{-1}\,\text{cm}^{-1}$, i. e. if the electron mean free path is greater than the mean interatomic distance;

ii) diffusive transport is expected for $2000\ \Omega^{-1}\,\text{cm}^{-1} \gtrsim \sigma \gtrsim 300\ \Omega^{-1}\,\text{cm}^{-1}$, where the density of states should become a dominating factor for the electron transport;

iii) for lower σ-values nonmetallic conduction should set in due to the occurrence of a mobility gap.

According to this approximate division the liquid alkalimetal-antimony alloys behave nonmetallic over most of the concentration range, roughly speaking for $0.15 \lesssim X_{Sb} \lesssim 0.85$ — see Figure 3. On the alkali metal rich side a σ-value of $\approx 2000\ \Omega^{-1}\,\text{cm}^{-1}$ around $X_{Sb} \approx 0.15$ coincides with a change in sign — from negative to positive — of the temperature dependence of σ. This seems to be a general characteristic of the lower end of the metallic transport regime and is observed during the M-NM transition in such different liquid systems like metal-chalcogen alloys [1] or expanded fluid alkalimetals [27], see also [28]. A transition to clearly nonmetallic states is demonstrated by the extremely sharp conductivity drop at the compound composition A_3Sb and by the behavior of the electronic properties on the antimony rich side of this composition.

In view of the questions raised in the introductory section the following observations are particularly noteworthy which give some evidence for semiconducting characteristics in the antimony based alloys similar to metal-chalcogen systems. This classification is based on the following features:

i) The strong concentration dependence of σ near the compound composition A_3Sb and the pronounced asymmetry of the isotherms about this composition are directly comparable with systems containing either Te or Se as one component — see e. g. [1] — and are not consistent with the observed behavior in predominantly ionic alloys like the Cs-Au system — see e. g. [4, 5].

ii) The same conclusion must be drawn from the absolute thermoelectric power S as a function of composition — see Fig. 4. The observed inversion in sign of S for $X_{Sb} > 0.25$ is typical of a number of liquid alloy semiconductors which are not characterized by an essentially ionic structure. It is indicative of both electron and hole contributions to S. This finding together with the monotonic increase of S towards relatively large positive values for the Sb-rich alloys may imply a continuous change in the electronic structure between the boundaries given by the compound compositions A_3Sb and ASb, respectively.

iii) Particularly striking is the strong positive temperature dependence observed in the electrical properties for $X_{Sb} > 0.25$, see Fig. 3 and Figure 4. This again shows a close similarity with a number of chalcogen alloys. In addition, clear indications for thermally activated transport processes are found — see also [15]. This is demonstrated in Fig. 7 for the example of the compound composition ASb. Over a limited temperature range of about 150 K above the melting point a T^{-1} dependence of $\ln \sigma$ is

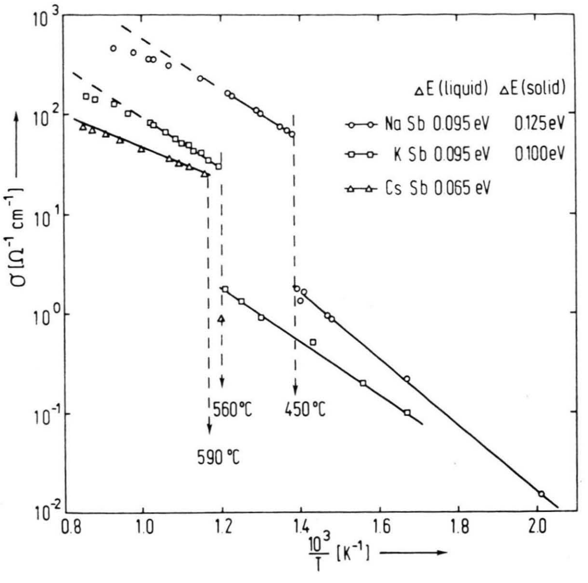


Fig. 7. Logarithmic plot of electrical conductivity, σ, vs. reciprocal temperature for alkali-antimony alloys with compound composition ASb (A = Na, K, Cs) in the solid and liquid state.

found with activation energies ΔE of comparable magnitude both in the solid and liquid state. The observed deflexion of the $\ln \sigma$ vs. T^{-1} curves for higher temperatures and for σ-values approaching $100 \ldots 200\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is reminiscent of the behavior found in pure fluid Se [29] and some chalcogen based systems [1].

With this background some conjectures on the change of the chemical bonding are possible whereby the results reported here and the further informations discussed below suggest a continuous variation in the electronic and the local molecular structure going from the A_3Sb to the ASb compound compositions. Concerning the solid compounds A_3Sb these are not predominantly ionic in character. This may be derived from the crystalline structures – see e. g. [11, 12] – and from several NMR studies [30, 31]. So a description of the solid by s-p-hydridized bonds [32, 33] or by a covalent partial lattice [33] has been suggested. In the liquid state an essentially ionic bonding may be excluded by a simple consideration of the magnitude of the magnetic susceptibility χ_m at the diamagnetic minimum at $X_{\mathrm{Sb}} = 0.25$ – see Figure 5. For mainly ionic interaction between A^+ and Sb^{3-} ions the estimated ionic susceptibilities [7, 15] in comparison with the corresponding experimental values near liquidus temperature – given in brackets – are: Na_3Sb, -24 (-17); K_3Sb, $-31(-17)$; Cs_3Sb, $-45(-20)$; (all numbers in units of 10^{-6} emu g-atom^{-1}). Although this consideration is highly qualitative the distinct deviations cannot be reconciled with an ionic model. There might be a trend towards slightly larger charge transfer in Na_3Sb relative to Cs_3Sb which might lead to more stable Na_3Sb compounds. This assumption fits in with the trend in the melting points of the A_3Sb compounds and might also explain the trend in the T-dependence of χ_m around $X_{\mathrm{Sb}} = 0.25$ which is smallest for the Na-alloys. In relation with a possible change of bonding or the amount of charge transfer during melting it is interesting to note that both χ_m and σ do not vary discontinuously for concentrations $X_{\mathrm{Sb}} = 0.25 \pm \delta$ (δ small) but only the slope of $\sigma(T)$ changes. This is in contrast to the behavior found around the stoichiometric composition ASb, see Figure 7. In summary we suggest that the bonding near the compound composition A_3Sb is determined by an ionic-covalent mixed bonding and not by an essentially ionic interaction. This description is also consistent with a recent thermodynamic investigation of liquid Cs-Sb alloys [34].

We shall now consider the antimony-rich alloys up to the concentration range of the ASb compounds. If one remembers that Sb^- is isoelectronic with Te it is not surprising that the electronic properties reported above are closely similar to the chalcogenide systems. Thus the formation of covalently bonded Sb-Sb chain structures has to be taken into account. This view is in good agreement with the published thermodynamic properties of these liquid alloys [35] and recent NMR-studies [36]. A direct experimental evidence for the existence of a covalently bonded antimony chain structure has recently been given by a neutron diffraction study of liquid Cs-Sb alloys for $X_{\mathrm{Sb}} \leqq 0.5$ [37]. For $X_{\mathrm{Sb}} = 0.35$ and 0.5, respectively, the pair distribution function shows a peak at 2.8 Å which directly correlates with the covalent Sb-Sb bond distance of the Sb-spiral chains in the corresponding solid ASb compounds. These have either monoclinic or orthorhombic structures, see e. g. [12]. In connection with these complex structures the large negative excess volume presented in Fig. 6 is not too unusual. On the other hand, this is the first example to our knowledge where such a rare volume contraction has been observed for a liquid alloy semiconductor which is not essentially ionic in character. The volume shrinkage of about 40% for $0.25 \leqq X_{\mathrm{Sb}} \leqq 0.5$ is of similar magnitude as in liquid Cs-Au alloys [19]. Commonly large negative excess volumes have been associated with a large ionicity.

In conclusion we may state that the liquid alkali-metal-antimony systems show many of the characteristics typically found in liquid chalcogen based semiconductors. For a discussion of the electronic structure of these alloys the consequences of this suggestion are obvious. We think that in comparison with a rigid band model type description which is successful in the Cs-Au system an approach similar to the bond orbital model proposed by Cutler [1] is more appropriate.

Acknowledgement

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