The Variation of Absorption Edges of X-Rays for Liquid Hg-Rb Alloys

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The L_I and L_{III} edges of Hg and the K edge of Rb in liquid Hg-Rb alloys were measured by the absorption spectroscopy of X-rays. On increasing the Rb concentration, the absorption edges of Hg show an opposite behavior each other, the decrease of L_I and the increase of L_{III} compared with the case of pure liquid Hg. This difference was discussed from the polyanion formation of Hg atoms on alloying. With the increase of alkali concentration, the p like state or polyanion seems to be situated on the lower energy side than that of s band. The electronic structure of this polyanion was discussed based on a simple LCAO analysis. Such an existence of polyanions may be responsible to the curious phenomena of liquid Hg-alkali alloys, the maximum of the electrical resistivity at 60 at% alkali and the positively enhanced tendency in the intermediate alkali concentration range of the magnetic susceptibility in the overall negative deviation.

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1. Introduction

In liquid alkali-polyvalent metal alloys, there exists a compound formation at some particular composition even in liquid alloys.^{1,2)} Such a typical system is liquid Pb-K alloy. In this system, at the composition of 50 at%K, the drastic increase of electrical resistivity occurs. This has been attributed to the formation of tetrahedral Pb_4^{4-} polyanion, whose chemical bond is considered to be a bonding orbit derived from the overlap of p orbits.¹⁻⁴⁾ The existence of this polyanion has been confirmed by the presence of a huge “prepeak” in the wave number range just before the first peak of the structure factor. Liquid mercury alloys, particularly liquid mercury-alkali alloys show also various curious phenomena, such as the minimum in the thermoelectric power, Q , at a few at% solute (“minimum in Q ” (see Fig. 1)),⁵⁾ the maximum of electrical resistivity at 60 at% alkali,⁶⁾ and the enhanced tendency in the intermediate concentration range of the magnetic susceptibility in the overall negative deviation tendency (“W shape” (see Fig. 2)).⁷⁻⁹⁾ The “minimum in Q ” appears for liquid alloys containing In, Tl, Li, Na, K, Rb, and Cs as a solute. Their phase diagrams¹⁰⁾ indicate many intermetallic compounds in the concentration range over 20 at% solute and there are no particular features around Hg-rich region of a few at% solute, at which the “minimum in Q ” appears. There are no indications to resolve the cause of its origin. The “minimum in Q ” was described as a “mysterious phenomena” in the previous textbook (Faber 1972).¹¹⁾

Up to date, as for the “minimum in Q ”, following points have been clarified by the author’s group.

- (1) “The minimum in Q ” appears in the mercury systems for which the heat of mixing is negative.⁵⁾
- (2) It appears for the systems in which the electronegativity (or work function) difference between components is large.⁵⁾

Fig. 1 The concentration dependence of the thermoelectric power, Q , for liquid Hg-alkali alloys.

- (3) It is accompanied by the anomalous behavior of the temperature (or pressure) coefficient of physical quantities, such as the temperature coefficient of the electrical resistivity, thermoelectric power, magnetic susceptibility, atomic volume, and viscosity, partial molar entropy, and the pressure coefficient of thermoelectric power.^{7,12,13)}

The points, (1) and (2), indicate that the “minimum in Q ” is caused by the charge transfer effect from solute (alkali) atoms to Hg ones. As is well known, the temperature coefficient and the pressure coefficient of the pair distribution function involve the three- and four-body distribution functions. Therefore the last point, (3), indicates that some local structure may appear due to this charge transfer effect. We presented the speculation that the “solvation structure” exists at a few at% solute in liquid Hg alloys for which the “minimum in Q ” can be seen. In this concentration range, positively charged alkali atoms may be surrounded with the partially charged Hg ones of negative sign. This situation is similar to the electrolyte water solution, in which the

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Fig. 2 The concentration dependence of the magnetic susceptibility, χ_M^e , for liquid Hg-Na, Hg-Rb, and Hg-Cs alloys. For liquid Hg-Cs alloys, the total magnetic susceptibility, which is derived from contribution of the conduction electrons (electronic part) and the ion core, is depicted and, for liquid Hg-Na and Hg-Rb alloys, only the contribution of electronic part is shown.

cation of, for example, Na^+ ion is surrounded with the oxygen atoms of water molecules, in which oxygen atoms possess a partially negative charge due to the polarization effect.¹⁴⁾

Thus, the charge transfer effect is essential for the understanding of the physical properties of liquid Hg-alkali alloys. This charge transfer effect may be also responsible to anomalous behaviors in the intermediate alkali concentration range, the maximum electrical resistivity at 60 at% alkali in common among all liquid Hg-alkali alloys, and the W shape of the magnetic susceptibility. In the previous paper,⁷⁾ a polyanion formation, such as Hg_4 unit, was speculated around 60 at% alkali. Up to date, such a polyanion formation in liquid Hg-alkali alloys has been discussed based on the analysis of EXAFS signal¹⁵⁾ by comparing the analyzed interatomic distance of Hg-Hg pair with that in the solid state obtained by the X-ray diffraction. It was also confirmed by the existence of the "prepeak" in the structure factor obtained by the neutron diffraction.¹⁶⁾ The Reverse Monte Carlo (RMC) analysis¹⁶⁾ of this structure factor also supports the existence of such polyanion. In this paper, such a polyanion formation is discussed from the X-ray absorption edge obtained in the European Synchrotron Radiation Facility (ESRF). Furthermore, this polyanion formation is supplemented by the discussion based on the linear combination of atomic orbitals (LCAO) method.

2. Experimental

The X-ray absorption spectra were measured for liquid Hg-Rb alloys at the BM29 beamline in the ESRF. The energy range of synchrotron X-ray was from the energy below the absorption edge of Hg L_I (14.839 keV), Hg L_{III} (12.284 keV)

Fig. 3 The assembly of glass (quartz) cell; (a): sample ampoule port; (b): furnace; (c): cock for Ar gas inlet; (d): glass (quartz) cell part; (e): window (aluminum) for the X-ray; (f): glass (quartz) cell part containing liquid Hg-Rb sample.

and Rb K (15.200 keV)¹⁷⁾ to 15.6 keV. In the preliminary stage of experiment, the full cross-section of rectangular shape was confirmed for the transmitted X-ray beam which passed through the window (4 mm diameter) of glass (quartz) cell in Fig. 3. The X-ray absorption edge was determined by the inflection point of the transmitted X-ray intensity.

Strictly speaking, measured spectra contain the contribution of glass cell. However, in the preliminary X-ray absorption experiment, the spectrum of the blank cell shows a monotonous decrease with a small absorption. Probably this may be explained by the fact that the absorption K edges of Si (1.838 keV) and O (0.531 keV)¹⁷⁾ of glass (quartz) cell were far distant from the energy range studied here. The effect of absorption of glass cell seems to be not so serious for the present study which is mainly concerned with the behavior of absorption edges for liquid Hg-Rb alloys.

The alloy sample was prepared in an Ar-circulating glove box by weighing and introduced into a glass ampoule, which, in the next stage, was contained in a glass cell whose optical path has a size of 20–150 μm length and 4 mm diameter. The glass ampoule containing the sample in the solid state was destroyed in the glass cell under a vacuum by adding the breaking force with the use of the screw. Then, the sample

Fig. 4 Concentration dependence of the normalized X-ray absorption spectra of liquid Hg-Rb alloys; (a): Hg L_{III} edge; (b): Hg L_I edge; (c): Rb K-edges. Positions of the absorption edges were indicated by arrows only in Fig. 4(a).

was melted and sufficiently homogenized in the liquid state. Finally, the liquid sample was introduced into the optical path region by Ar pressure. Figure 3 shows the assembly of the glass (quartz) cell, in which the broken glass ampoule containing a solid sample is schematically depicted. The experimental temperature was 50 K higher than the melting point.

3. Results

The obtained absorption spectra are shown in Fig. 4. These spectra show interesting behaviors on alloying, the decrease of the absorption edge for Hg L_I and Rb K and the increase of that for Hg L_{III}. There exist several methods for the

determination of the absorption edge.^{18,19)} Following to Lee *et al.*,¹⁹⁾ the inflection point was adopted as the absorption edge in this study, as shown by arrows in the L_{III} edge in Fig. 4(a). Similar tendencies could be observed for the variation of the absorption edge on alloying even if it was determined by the energy of initial increase or that of the first maximum on the curves of absorption versus energy in Fig. 4.¹⁸⁾

The change of the absorption edge is very small compared with the energy of the incident X-ray. We noted the energy shifts of the absorption edges of liquid Hg-Rb alloys compared with those of pure liquid Hg and Rb, as shown in Table 1. Obtained energy shifts in the concentration range of 35–92 at% Rb were expressed as follows:

$$\begin{aligned} \Delta E_0 &= 0.00797x - 0.698, & \text{for Rb } K \text{ edge;} \\ \Delta E_0 &= 0.00188x - 1.403, & \text{for Hg } L_I \text{ edge;} \\ \Delta E_0 &= 0.0114x + 1.574, & \text{for Hg } L_{III} \text{ edge.} \end{aligned}$$

In these equations, x is the concentration of Rb in at%.

4. Discussions

As can be seen in Table 1, it is very interesting that on alloying the Hg L_I edge decreases and the Hg L_{III} one increases. So far as authors know, such interesting behaviors of the absorption edge have been rarely reported for alloys in the solid state and the liquid state. The selection rule of this electron transition process is $\Delta l = \pm 1$,²⁰⁾ which means that the difference of azimuthal quantum number, l , of electrons should be ± 1 between the initial state and the final one. The L_I edge corresponds to the electron transition from the initial state of 2s inner core state to the final one of p type and the L_{III} edge to that from the initial state of 2p core state to the final one of s type. In principle, the absorption edge should depend on the energy of both the initial state and the final one. However, for the absorption edges obtained in the present study, the final state around conduction band may be more deeply influenced on alloying compared with the initial one of deep core 2s and 2p states. Thus, the change of the

Table 1 The concentration dependence of the energy shifts of the X-ray absorption edges in liquid Hg-Rb alloys compared with those in pure liquid Hg and Rb.

Rb at%	Rb <i>K</i>	ΔE_0 (eV)	
		Hg L _I	Hg L _{III}
0		0	0
35	−0.53	−1.64	1.82
37	−0.42	−1.23	2.06
48	−0.25	−1.17	2
48	−0.26	−1.27	2.29
53	−0.21	−1.11	2.18
57	−0.17	−1.23	2.39
59	−0.41	−1.39	2.13
70	−0.06	−1.23	2.42
75	−0.18	−1.48	2.41
82	0.12	−1.29	2.56
92	0.02	−1.16	2.54
100	0		

absorption edge of Hg on alloying indicates that with the addition of alkali atoms the p like state becomes stable and the s like one unstable. This reasoning seems to be not inconsistent with the experimental fact, the decrease of Rb K edge (transition from initial 1s state to final p type one) on alloying, shown in Table 1.

With the addition of alkali atoms into liquid Hg, the distance between Hg atoms may increase. It is probable that the positively charged monovalent alkali ions do not contribute to the structure of energy band but only increase the sample volume or Hg-Hg distance. The increase of the energy of the final s like state or s band on alloying may be understood by the increase of the Hg-Hg distance, though this discussion depends slightly on the atomic distance dependence of band shape. However, it is very difficult to understand the decrease of the energy of the final p like state on alloying, if this p like state is derived from the 6p band. Usually the 6p band is situated on the higher energy side compared with the 6s band even if they overlap each other. Authors consider that this stabilization of final p like state is caused by the formation of atomic group of Hg atoms, polyanion, whose existence was confirmed as Hg_4 planar unit in the solid Hg_4Na_6 compound²¹⁾ and Hg_n ($n = 4$ or 5) unit in the solid $\text{Rb}_5\text{Hg}_{19}$ ²²⁾ by the X-ray diffraction analysis. For liquid Hg-alkali alloys, we stress the appearance of “inverse separation” of 6s band and 6p state of Hg_4^{6-} polyanion. The energy of 6p state of Hg_4^{6-} polyanion is inversely in the lower energy side than that of 6s band.

Here we note the existence of common composition of alkali concentration, 60 at% alkali ($\text{Hg}_4(\text{Alkali})_6$), at which the maximum of the electrical resistivity are observed on its isotherms for liquid Hg-alkali alloys. It is plausible to consider that the polyanion of Hg_4^{6-} type may be responsible to this maximum of the electrical resistivity. Probably this polyanion is formed by only one part of Hg atoms among all Hg ones. In addition, the electrical conduction in liquid Hg-alkali alloys is still carried out by the existence of vacant energy state in the overlapped sp band. The maximum of the electrical resistivity at 60 at% alkali may be caused by the reason that the polyanion of Hg_4^{6-} works as the strong scattering center against conduction electrons and its formation decreases the number of conduction electrons in the overlapped sp band.

As already described, the charge transfer from alkali atoms to Hg ones is the most fundamental factor to understand the curious physical properties of Hg-alkali alloys. With the proceed of charge transfer along with the increase of alkali concentration, the structure feature of liquid Hg-alkali alloys changes from the “solvation” structure to the “polyanion” one, Hg_4^{6-} . There are two possibilities for the structure of Hg_4^{6-} unit, planar square and tetrahedron. For the planar square array of p_z orbitals, a simple LCAO analysis provides one $p\pi$ bonding orbit, one $p\pi$ anti bonding one, and two $p\pi$ non-bonding orbitals.²³⁾ The bonding orbitals of the planar square array are four $p\sigma$ orbitals and one $p\pi$ orbit. The Hg_4^{6-} unit has six p electrons which are transferred from alkali atoms. The occupied ratio of their bonding orbitals is 0.6. In the case of tetrahedral configuration, there are six $p\sigma$ orbitals,²³⁾ whose occupied ratio is 0.5. Therefore, the planar square configuration seems to be more stable than the tetrahedral

one, though, strictly speaking, the energy must be discussed. In addition, the existence of polyanion seems to be supported by the W shape of the magnetic susceptibility (Fig. 2), because the partial occupation of bonding orbitals may enhance the paramagnetism. The existence of the Hg_4 units in liquid Hg-alkali alloys has been quite recently speculated in the quantum mechanical computational study,²⁴⁾ though the calculation has been performed not for the condensed phase but for the Hg-alkali diatomics.

In the present study the polyanion formation was confirmed from the behaviors of X-ray absorption edges. The oscillation of absorption spectra also provides important information for such polyanion formation. In fact, it has been reported^{15,16)} that the Hg-Hg distance, 295 pm, obtained from the analysis of EXAFS oscillation for liquid Hg-Rb alloys is in good accordance with that, 292 pm, given by the X-ray diffraction analysis for solid $\text{Rb}_5\text{Hg}_{19}$,²²⁾ for which Hg_n unit has been reported. Thus, in the intermediate alkali concentration range in liquid Hg-alkali alloys, the polyanion formation was confirmed also from the EXAFS study. Though the most advanced experimental tools, EXAFS, neutron scattering and the RMC were quoted for the present discussion, the discussion remains to be not so clear. This is caused by the moderate polyanion formation in the present liquid Hg-alkali alloys and the limitation of probabilistic nature of discussions for liquid state. The concentration of polyanion should be determined to make the present conclusion clear. For this purpose, the temperature dependence of NMR Knight shift and the heat of mixing are expected to be studied for liquid alkali alloys together with their theoretical analysis.

5. Conclusions

The X-ray absorption edge for liquid Hg-Rb alloys provided some evidence of polyanion formation, which is responsible to the curious physical properties of liquid Hg-alkali alloys in the intermediate alkali concentration range.

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