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An NMR study on the liquid caesium–oxygen system: the state of oxygen and ionic association in the metallic regime

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Abstract. The liquid caesium–oxygen system in the metallic regime has been investigated by the NMR technique. Measurements were made of the Knight shift for both ^{133}Cs and ^{17}O nuclei, and the nuclear relaxation time, T_1 , for the latter. The Knight shift for ^{133}Cs nuclei decreases almost linearly up to 25 at.% of O and further decreases with a steeper slope to the value in Cs_2O , while the shift for ^{17}O nuclei is almost independent of the composition up to 21 at.%. The analysis of T_1 suggests that the gradient of the electrostatic field coupled with the nuclear quadrupole moment of ^{17}O is also insensitive to the composition. The results are discussed with particular reference to the state of the O atoms and possible ionic association in the liquid Cs–O system in the metallic regime.

1. Introduction

Among a number of metal–oxygen systems, the caesium–oxygen (Cs–O) and rubidium–oxygen (Rb–O) systems have exceptionally low liquidus temperatures over a wide range of O composition. The metallic character of the liquids on the Cs-rich side has been shown by measurements of electrical conductivity (Brauer 1947). Besides the electrical conductivity, the Hall coefficients and density of Cs–O alloys up to 18 at.% of O (Kendal 1970) and the Knight shift of ^{133}Cs nuclei in a specimen with 12 at.% of O (Host *et al* 1970) have been reported. It has been suggested from these measurements that O exists as the O^{2-} ion. The radial distribution function determined by neutron diffraction experiments (Simon 1979a) shows that the Rb–O distance in liquid Rb_6O is similar to that in the solid compound Rb_6O . The Raman scattering spectra of Cs_7O preserve their characteristic features upon melting (Simon 1979b). Since an O atom exists as an O^{2-} anion in the solid suboxides, those results also suggest the O^{2-} state of O in liquid Cs, although the information from these measurements is rather indirect. To confirm the O form dissolved in liquid Cs, as well as to clarify the electronic structure of the liquid Cs–O system, therefore, more detailed study would be desirable.

Nuclear magnetic resonance (NMR) experiments provided an opportunity for gaining information on the local environment around probe nuclei. This is possible through measurements of the Knight shift and the spin–lattice relaxation time of respective nuclei in an alloy. The Cs–O system is very suitable because both ^{133}Cs and ^{17}O nuclei exhibit strong signals due to their large magnetic moments although the isotopic abundance of ^{17}O in natural O_2 gas is very low. The latter deficiency may be overcome by using a ^{17}O -enriched O gas in the sample preparation, however.

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So far large deviations from nearly-free-electron (NFE) behaviour have been observed in alkali metals alloyed with metallic elements having large electronegativity. Typical examples are Cs–Au and Cs–Sb, both of which undergo the non-metal–metal transition as the stoichiometric compositions (CsAu and Cs₃Sb, respectively) are approached (see, for example, Hensel 1979). The dependence on the excess Cs fraction of the electronic properties indicate that there is a qualitative difference in their chemical bonding. It has been suggested that this may be caused by a difference in the bound state formed at the electronegative ions, which has s character for Au and p character for the Sb ion. Thus it would be of some interest to investigate the change in the electronic structure due to the addition of O because the bound state, if it were formed in the liquid state, would have p character.

In this paper, we report an NMR study of ¹³³Cs and ¹⁷O nuclei in the liquid Cs–O system in the NFE transport regime. To supplement the NMR investigation, we have also measured the magnetic susceptibility and the electrical resistivity.

2. Experimental details

2.1. Sample preparation

Specimens were made by direct reaction of metallic Cs and low-pressure dry O gas in the ampoule used for the measurements. The metallic Cs is very reactive with moisture as well as O₂ in the air, so the whole procedure of preparing a specimen was carried out in an evacuated glass tube. The Cs from Koch-Light Co. Ltd was first divided into a few small glass ampoules with breakable tips by distillation. Next the total weight of the glass ampoule plus Cs was measured, then the Cs was distilled into another ampoule for measurements and the empty ampoule was weighed to determine the net amount of Cs. A typical amount of Cs for measurements was about 0.2 g and the accuracy of weighing was better than 1%. The apparatus used to add O to Cs was almost the same as that reported by Kendal (1970). The O₂ pressure was measured with a Burden gauge calibrated to a mercury manometer. The amount of O was determined with the volume of the O₂ reservoir and its pressure corrected for the temperature. After introducing O to the Cs, the pressure quickly fell to zero, indicating the complete reaction of Cs and O.

2.2. Resistivity measurements

Resistivity was measured with a standard four-terminal DC method using tungsten electrodes, which were sealed into a Pyrex glass cell and electrically etched to remove the surface oxide layer. The cell had a greaseless tap, which enabled the successive addition of O to a specimen. To keep Cs evaporation as small as possible, the cell was filled with argon gas, which was purified by passing through a titanium sponge kept at 700 °C and a molecular sieve. Thermoelectric and asymmetric contact effects were eliminated by averaging the readings for both current directions. The resistivity was determined with reference to the value for distilled Hg at 20 °C (95.8 μΩ cm).

2.3. Magnetic susceptibility measurements

Sealed samples in Pyrex glass ampoules were used for both magnetic susceptibility and NMR measurements. The magnetic susceptibility was measured with the usual Faraday method using five-nine grade silver as a reference, the susceptibility of which was taken as $-0.181 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. The measurements were carried out at several magnetic field strengths

between 0.8 and 1.24 T to eliminate effects due to contamination by magnetic impurities in the glass. It was found that the force acting on a specimen was not reproducible when the temperature was raised above about 350 °C, which would be indicative of the reaction of Cs and glass. Measurements were therefore restricted to temperatures below 350 °C.

2.4. NMR measurements

Measurements were made of the Knight shifts for the ^{133}Cs and ^{17}O resonance and spin lattice relaxation time T_1 for the ^{17}O resonance. The ^{133}Cs signal was measured for bulk non-dispersed specimens in which the signal from ^{133}Cs nuclei in the region of the RF skin depth was detected. The Knight shift was determined from the off-resonance free induction decay with respect to the signal from the solid Cs_2O at 7 MHz. The field strength was simultaneously determined by observation of the deuterium resonance in heavy water. Most of the measurements were carried out on a specimen in a cell with a greaseless tap, which enabled the O composition to be changed successively. In this case the temperature was limited to less than 200 °C to avoid the evaporation of Cs. Specimens sealed in Pyrex glass ampoules were also measured for the higher temperatures. To obtain the signal from ^{17}O , isotopically enriched O_2 gas was used with an isotopic abundance of 30% ^{17}O . The specimen was dispersed in dry paraffin oil after reaction of Cs and O. The O composition in a specimen was determined by measuring the Knight shift for ^{133}Cs . The resonance for ^{17}O was detected at 22 °C with a Varian*VF 16B NMR spectrometer operated at about 8 MHz. The shift was calculated with respect to the resonance position of ^{17}O in distilled water. T_1 values for ^{17}O were measured at Ames Laboratory, Iowa State University, USA.

3. Results

3.1. Resistivity

The resistivity is plotted as a function of temperature for compositions up to 27 at.% of O in figure 1. The very large temperature dependence for the $\text{Cs}_{73}\text{O}_{27}$ specimen might be due to evaporation of Cs and a resultant increase of O composition in the specimen during the measurements. The composition dependence at 140 °C has been plotted in figure 2. Agreement with the previously reported data is reasonable in the overlapping composition region (Brauer 1947, von Bauhofer and Simon 1978a). The resistivity as a function of O composition increases rather linearly up to 22 at.%. With a further addition of O, it increases with a much larger slope. The increase due to an addition of 1 at.% of O to pure Cs is $3.9 \pm 0.2 \Omega \text{ cm}$, which is in good agreement with a theoretical calculation (Greenwood and Ratti 1972).

3.2. Magnetic susceptibility

The dependence on temperature of the magnetic susceptibility, χ , is shown in figure 3. (Throughout this paper, except where otherwise stated, the symbol χ will be used to mean the molar susceptibility and values of χ will be given in units of centimetres cubed per mole. Where volume susceptibilities are used, they will be denoted by the symbol χ^V .) The value for pure Cs at the melting point is in good agreement with Collings' value (1965) but is smaller than that reported by Freyland (1979) by $2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, although the temperature dependence is in good agreement with that given by the latter. On adding O, the temperature coefficient of χ gradually decreases and becomes almost constant for specimens containing more than 10 at.% O.

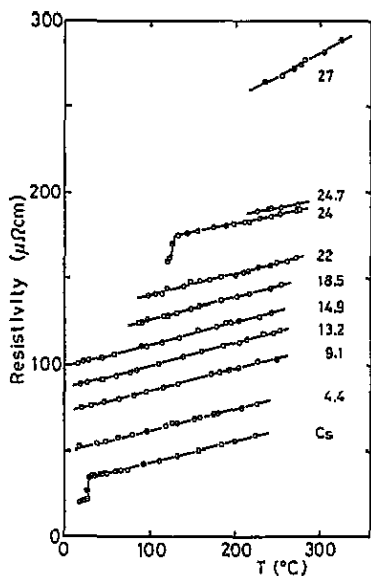


Figure 1. The resistivity for the liquid Cs-O system as a function of temperature. The numbers in the figure indicate the atomic percentages of O in the specimens.

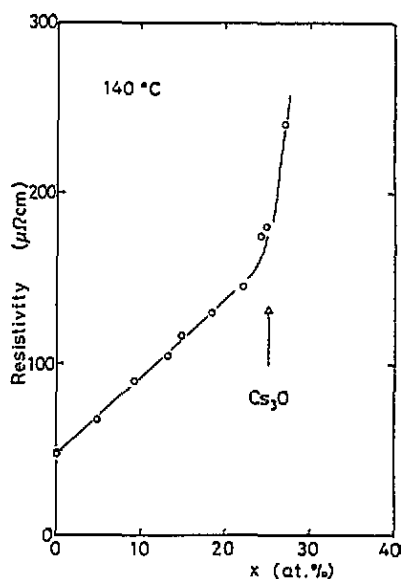


Figure 2. The resistivity isotherm for the liquid Cs-O system at 140°C .

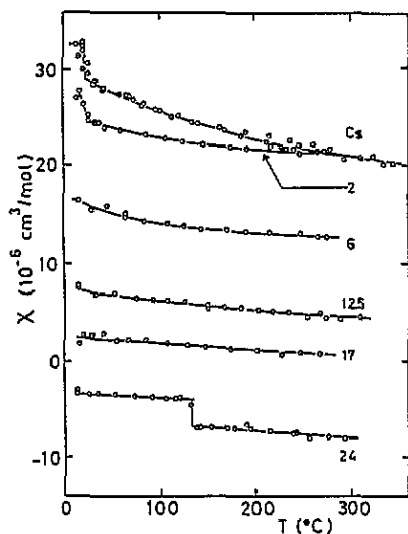


Figure 3. The magnetic susceptibility for the liquid Cs-O system as a function of temperature. The numbers in the figure indicate the atomic percentages of the specimens.

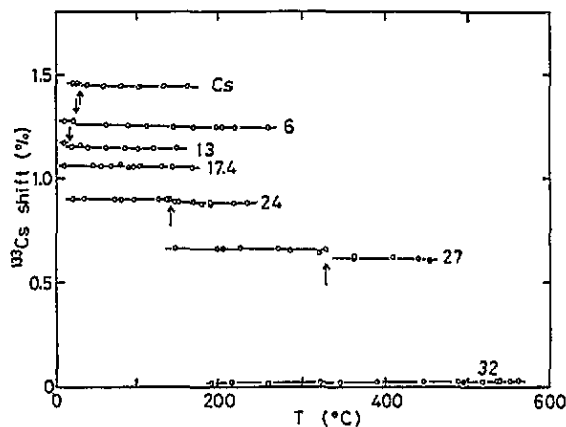


Figure 4. The ^{133}Cs shift in several Cs-O alloys as a function of temperature. The arrows indicate the liquidus points. The numbers in the figure are the atomic percentages of O in the specimens.

3.3. NMR

The Knight shift, which was determined with respect to the resonance peak in solid Cs_2O in several Cs-O alloys, is plotted as a function of temperature in figure 4. At the liquidus

temperature, the shift decreases stepwise, although the step is hardly recognizable in the figure. In the liquid state, the shift decreases linearly within experimental uncertainty. Figure 5 shows the shift as a function of O composition, where the data were taken at 140 °C unless otherwise indicated in the figure. The overall profile of the shift versus composition curve is insensitive to the temperature. The Knight shift decreases almost linearly up to 24 at.% of O and further decreases with a steeper slope to the value in Cs_2O . Consequently a characteristic inflexion occurs around the O composition corresponding to the stoichiometric compound Cs_3O .

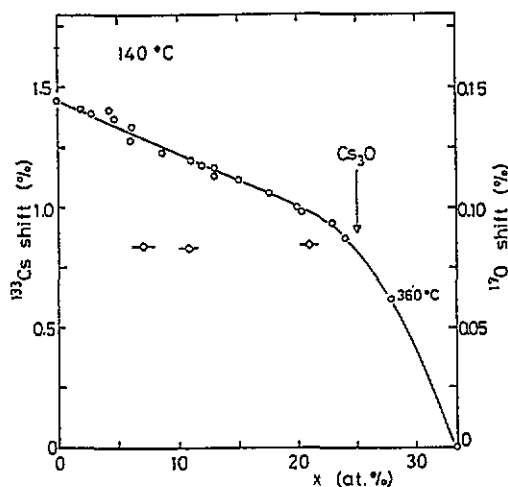


Figure 5. The ^{133}Cs shift at 140 °C (O) and the ^{17}O (\diamond) at 22 °C as a function of O composition. The data for solid Cs_2O are at room temperature.

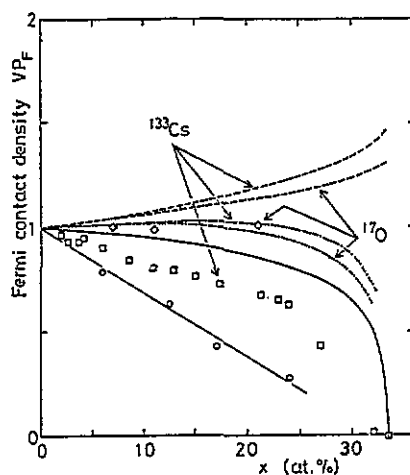


Figure 6. The broken curves show single OPW calculations of the Fermi contact density, VP_F , for ^{133}Cs and ^{17}O as a function of O composition. The solid curve indicates the variation of the free-electron Pauli volume susceptibility. The chain curves are for the theoretical variation of the Knight shift for the respective nuclei obtained from these two quantities. Experimental results for the ^{133}Cs shift (\square), ^{17}O (\diamond), and electron volume susceptibility, χ_e^V , (\circ) are also shown. All the data are normalized to pure Cs.

In contrast the Knight shift for ^{17}O at 22 °C is almost independent of the O composition as listed in table 1 and also plotted in figure 5. The shift of ^{17}O has a surprisingly large value, which is comparable with the value of 0.116% for ^{23}Na in liquid Na (Dupree and Seymour 1972).

4. Discussion

The resistivity isotherm in figure 2 indicates that the Cs-O system keeps its metallic character and remains as a good conductor up to about 25 at.% of O, the resistivity of which is less than $200 \mu\Omega \text{ cm}$. Therefore an NFE model would be a good starting point for discussing the present magnetic data.

Table 1. The ^{17}O Knight shift K (%), the spin-lattice relaxation time T_1 (ms) and the calculated quadrupole relaxation time T_{1q} (ms). $\Delta K/K$ is about 1.2%.

T ($^{\circ}\text{C}$)	7 at.% O		11 at.% O		21 at.% O		
	K	K	T_1	T_{1q}	K	T_1	T_{1q}
20.6	0.0844	0.0832	23	2.5	0.0849	11.4	12
22	—	0.0832	—	—	0.0864	—	—
83	—	—	—	—	—	32	40
128	—	—	90 ± 5	160	0.0881	79	180
140	—	0.0808	—	—	0.0869	—	—
160	—	—	—	—	0.0891	105	515

First we mention the temperature dependence of the magnetic susceptibility χ of pure Cs. We assume that χ may be written in the conventional form,

$$\chi = \chi_i + \chi_e = \chi_i + \chi_d + \chi_p \quad (1)$$

where χ_i is the temperature-independent diamagnetic susceptibility of the ion cores ($-36.0 \text{ cm}^3 \text{ mol}^{-1}$ for Cs^+ and $-12.0 \text{ cm}^3 \text{ mol}^{-1}$ for O^{2-} (Dupree and Seymour 1972)) and χ_e the contribution from the conduction electrons. The latter consists of the Pauli paramagnetic and the Landau diamagnetic susceptibility, denoted as χ_p and χ_d , respectively. The temperature dependence of χ_e may be divided in two parts. One is the effect brought about by the volume expansion and the other the residual explicit temperature effects at constant volume. It is expected from free-electron theory that the volume expansion causes the increase of χ_e and hence the total susceptibility, χ , if the effect of the volume change on the exchange enhancement of χ_p is small and if χ_d follows the elementary theory. For most simple liquid metals, χ increases with the temperature in accord with this prediction and the explicit temperature effect is supposed to be small (Faber 1972). In contrast, as shown in figure 3, χ of liquid Cs decreases with increasing temperature. It has been shown from the temperature-pressure dependence of the Knight shift that the volume dependence of χ_e for Cs at constant temperature obeys the prediction of simple free-electron theory (Warren *et al* 1989). Thus the decrease of χ of liquid Cs may be ascribed to the temperature effects at constant volume. So long as no change in volume is concerned, the most plausible temperature effect is thermal averaging of the structure, which would make the local atomic arrangement more isotropic and result in a tendency toward a more free-electron-like density of states with increasing temperature. Calculations of the density of states (Halder 1973) and the magnetic susceptibility (Takahashi and Shimizu 1973) suggest that the thermal averaging of structure in fact plays an important role. However, more detailed study seems to be required to clarify the origin of the temperature dependence of χ for liquid Cs.

The Knight shift is given by the following usual form,

$$K = (8\pi/3)\chi_p^V V P_F. \quad (2)$$

Here χ_p^V is the paramagnetic contribution to the electron susceptibility per unit volume and P_F is the Fermi contact density. To obtain an insight into the dependence on O composition of the Knight shift theoretical values of $V P_F$ in (2) have been estimated by a single orthogonalized plane-wave (OPW) calculation on the following assumption: each added O preserves two electrons from the conduction-electron gas in forming an O^{2-} ion and assuming that the average volume per atom is $xV_A + (1-x)V_B$ where V_A and V_B are

the atomic volumes of the free O and Cs ion respectively. This naive presumption explains the composition dependence of the Hall coefficient of the liquid specimens (Kendal 1970), and the width of the conduction band and plasma frequency for metallic Cs suboxides (Ebbinghaus and Simon 1970). In the OPW calculation, the numerical wave functions of Herman and Skillman (1963) were employed. Since the calculation is too simple to predict the absolute magnitude of the Knight shift, the results normalized to pure Cs are shown in figure 6. The Fermi contact density, VP_F , for both nuclei increases with O composition mainly due to the decrease of the screening effect of the ionic potential. The electron susceptibility per unit volume, χ_e^V , deduced from the magnetic susceptibility and the free-electron paramagnetic susceptibility, both of which are normalized to the Cs value, are also plotted in the same figure. Since the actual paramagnetic susceptibility, χ_p^V , would also decrease in a similar fashion, OPW calculations suggest the following two points: (i) the composition dependence of the ^{133}Cs shift is dominated mostly by the reduction of the paramagnetic susceptibility, χ_p^V , associated with the decrease of conduction electron density caused by adding O and (ii) the observed constancy of the ^{17}O shift is perhaps caused by the cancellation of the contributions from VP_F and χ_p^V .

The nuclear spin relaxation time T_1 may bring useful information on the local structure around an O nucleus. In table 1, we have listed the spin–lattice relaxation time T_1 for ^{17}O at several temperatures. The spin–lattice relaxation time in the liquid metal normally consists of two terms (see, for example, Dupree and Seymour 1972)

$$1/T_1 = 1/T_{1e} + 1/T_{1q} \quad (3)$$

where T_{1e} arises from the interaction between conduction electrons and the nuclear dipole. T_{1q} is the quadrupole relaxation time associated with the relaxation process due to the interaction of the nuclear quadrupole moment, Q , with its surrounding electrostatic field gradient, q . The former can be estimated with the so-called modified Korringa relation in terms of the Knight shift (Dupree and Seymour 1972). We assume that the enhancement factor involved in the modified Korringa relation is the same for both ^{133}Cs and ^{17}O to a first approximation, because it depends only on an electron–electron interaction in an electron gas. By combining these estimates of T_{1e} with experimental values of T_1 an estimate of T_{1q} can thus be obtained. These are also listed in the table 1. In the extreme narrowing limit, we have

$$1/T_{1q} = [3\pi^2(2I + 3)/10I^2(2I - 1)] \overline{(e^2Qq/h)^2} \tau_q \quad (4)$$

where I is the nuclear spin quantum number. Since the correlation time τ_q is supposed to decay exponentially with the reciprocal of temperature, we expect a linear relation between $\ln(1/T_{1q})$ and $1/T$ for constant $\overline{(e^2Qq/h)^2}$. As plotted in figure 7, all points appear to fall on a common line with a slope corresponding to 26 kJ of activation energy for τ_q . $1/T_{1q}$ decreases with temperature very much more rapidly than the reciprocal of the self-diffusivities (Sholl 1967) for which the activation energy in liquid alkali metals falls between 8 and 12 kJ, although no experimental data seem to be reported for liquid Cs (Iida and Guthrie 1988). It may be concluded from this plot that $\overline{(e^2Qq/h)^2}$ in both mixtures has almost the same magnitude or in other words the local environment around O ions is insensitive to the composition. Such a situation would be expected if the dissolved O formed some association rather than a random mixture. Although we could not find a report on a liquid Cs–O mixture, the neutron scattering experiment on liquid Rb_6O shows that a well defined prepeak appears at 0.68 \AA^{-1} , which corresponds to pair correlations as long

as 9.2 Å in real space, and the pair correlation function preserves characteristic features of the ionic clusters in the solid suboxide (Simon 1979a). A similar very pronounced prepeak has been found at 0.72 \AA^{-1} in the scattered x-ray intensity of a glassy sample Cs_4O (von Bauhofer and Simon 1978b). Moreover the Raman spectra of solid and liquid Cs_7O are very similar and the characteristic bands in the spectra of the liquid appear to correspond to internal modes of the weakly perturbed 'molecular' clusters, although assignment of the bands to definite vibrational modes have not yet been made (Simon 1979a,b). All these experimental results also lead to the conclusion that Cs-O association similar to that in suboxides remains after melting. The very large Knight shift of ^{17}O suggests that there is substantial penetration of the conduction electron charge into the nucleus of the O^{2-} ion and thus the presumed ionic association is metallic in its character.

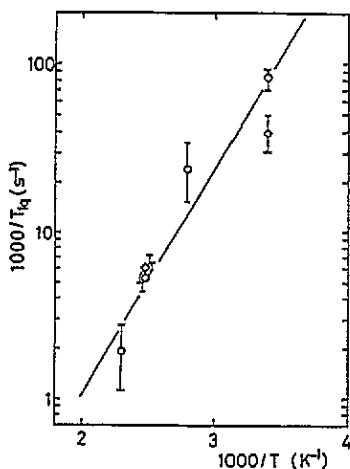


Figure 7. $1/T_{lq}$ as a function of the reciprocal of temperature, $1/T$. Circles and diamonds are the data for $\text{Cs}_{89}\text{O}_{11}$ and $\text{Cs}_{79}\text{O}_{21}$, respectively.

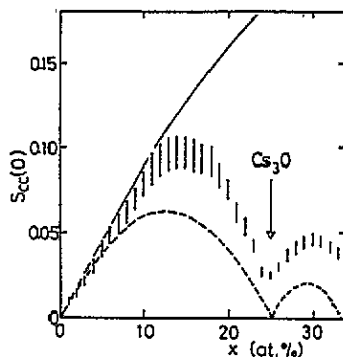


Figure 8. Concentration-concentration fluctuations, $S_{cc}(0)$, at 500 °C estimated from EMF data of Knights and Phillips (1979). The solid curve is $S_{cc}(0)$ for random Cs-O mixtures, and the broken curve is the model $S_{cc}(0)$ for Cs-Cs₃O and Cs₃O-Cs₂O mixtures.

The Cs-O system has a few stoichiometric suboxides between Cs and Cs_2O (Knights and Phillips 1979). All of them are known to be metallic in their electric properties. It is of interest to consider the type of association that may survive after melting. The concentration-concentration fluctuations at the long-wave-number limit, $S_{cc}(0)$, offer a clue to this question. In figure 8, we have plotted $S_{cc}(0)$ at 500 °C deduced from the EMF data of Knights and Phillips (1979). There appears to be interesting structure in the $S_{cc}(0)$ versus composition curve: $S_{cc}(0)$ has a minimum around Cs_3O and becomes very small at Cs_2O after going through the second maximum between these two compositions. We have also plotted a model $S_{cc}(0)$ curve, which would be expected for the ideal pseudo-binary mixtures of Cs-Cs₃O and Cs₃O-Cs₂O in the corresponding composition ranges. These results suggest that atomic association having a structure similar to Cs_3O persists up to 25 at.% of O. In the solid phase all the suboxides up to Cs_3O consist of O atoms surrounded by octahedra of Cs atoms and excess 'free' Cs atoms. In Cs_3O the latter are just expended (Simon 1979a). In Cs_2O , the metallic nature is lost by completing the chemical valence requirements and the octahedral unit is no longer stabilized (Wyckoff 1965). The characteristic inflection around

25 at.% O in the resistivity and the ^{133}Cs shift as a function of composition in figures 2 and 5 may be interpreted as an indication of similar structural evolution in the liquid.

So far Cs–Au, Cs–Sb and Cs–I systems have been studied by means of NMR over the full range of the non-metal–metal transition (Dupree *et al* 1980, 1982, Sotier and Warren 1980). When the Knight shift is plotted against the excess Cs fraction, differences appear as seen in figure 9. (Note that the abscissa for the Cs–O alloy is different.) The dotted curve in the figure gives the free-electron paramagnetic volume susceptibility normalized to pure Cs. As is clearly seen, there is no agreement between this model and the experimental results for the Cs–Sb system, while this type of comparison can reproduce the overall characteristic feature for the Cs–Au system. The disagreement with the free-electron model is also obvious for the Cs–O system as compared in figure 6.

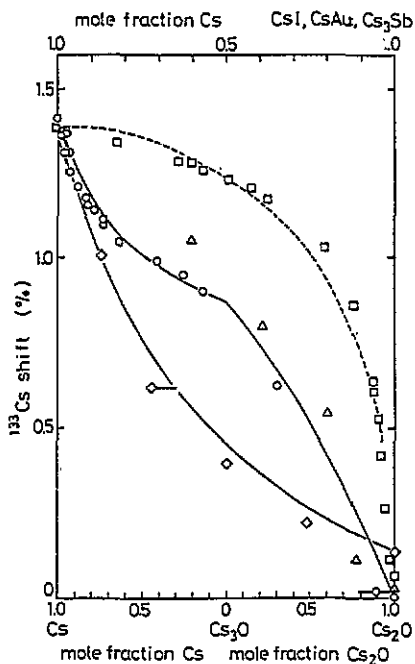


Figure 9. ^{133}Cs shift as a function of the excess Cs fraction: Cs–O (○) at 140 °C; Cs–Au (□) at 600 °C (Dupree *et al* 1980); Cs–Sb (◇) at 700 °C (Dupree *et al* 1982) and Cs–I (Δ) at 640 °C (Sotier and Warren 1980). The broken curve is the free-electron Pauli paramagnetic volume susceptibility normalized to pure Cs. The solid curves show the predictions of equation (5).

Having in mind the structural evolution mentioned in the preceding paragraph, we consider the case where the interaction between Cs and dissolved electronegative element is strong enough to affect the Fermi contact term for the Cs nuclei adjacent to a dissolved atom but still the exchange between bound Cs and free Cs is fast enough to establish the motional narrowing. In this case the resonance shift may be given by the following equation to a crude approximation:

$$K = K^f - (K^f - K^b)x/(1 - x)v/\mu$$

or

$$K = K^f = (K^f - K^b)v(1 - y)/[v - (v - 1)y] \tag{5}$$

where x and y are the fraction of the dissolved element and the excess Cs fraction, respectively. A type of Cs_vA_μ association (where A is the electronegative element) is

assumed, and K^f and K^b are the shifts for free and bound Cs, respectively. As plotted in figure 9, this simple model can reproduce the gross feature of the Knight shift as a function of the excess Cs fraction for the Cs–O and Cs–Sb systems where $\nu = 3$ and $\mu = 1$ are assumed. Similarly a mixture of Cs₃O- and Cs₂O-type associates appears to reconcile with the composition dependence for $25 < x < 33.3$ at.% O. These results are quite consistent with $S_{cc}(0)$ plotted in figure 8 as well. For the Cs–Sb system, the formation of molecular units of Cs₃Sb has been suggested (Dupree *et al* 1982). Thus the phenomenological resemblance in the Knight shift versus excess Cs fraction curve may also support the persistency of Cs₃O association in the liquid Cs–O system. The observed differences among these Cs mixtures would be attributed to whether or not molecular units form in liquid Cs and presumably to the character of the bound state at the electronegative elements.

In conclusion, we have studied the properties of Cs–O mixtures by measuring the electrical resistivity, magnetic susceptibility and Knight shift. The formation of Cs₃O units is concluded in the liquid Cs–O system of the NFE transport regime. the O²⁻ state suggested is compatible with the present observation.

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