Structure of Molten Mg, Ca, Sr, and Ba by X-ray Diffraction

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X-ray diffraction patterns have been measured on molten alkaline earth metals (Mg, Ca, Sr, and Ba) in the temperature range from the melting points to 880 °C. In all cases the structure factors obtained were temperature insensitive. By the usual Fourier transformation of the structure factors, the atomic radial distribution functions were evaluated. From these the interatomic distances and coordination numbers were estimated. The structural information was applied to a discussion of the electron-transport properties using the Ziman theory.

1. Introduction

Many experimental and theoretical studies have been performed on various properties of molten metals[1]. For the quantitative discussion of these properties the knowledge of the structure is indispensable. The alkaline earth metals are important because they are precursors of the transition series. To the author's knowledge, however, only diffraction data on magnesium in the molten state have as yet been reported.

In this work the structure of the molten alkaline earth metals at several temperatures has been measured by X-ray diffraction. From this structural information, using Ziman's theory, the electrical resistivity and thermoelectric power were calculated and compared with experimental data of Van Zytveld, Enderby and Collings[2, 3].

2. Experimental Procedures

The experimental arrangement and operating procedure for the X-ray measurements on high-temperature melts have been fully discussed in[4, 5]. All data were obtained with a combination of Mo and Cu radiations. The intensity was measured stepwise as a function of the scattering angle 2θ over the range $2\theta = 4°$ to $130°$. A graphite monochromator was installed in the diffracted beam to eliminate extra radiations such as white spectrum, K_β-radiation, most of the Compton scattering and fluorescent radiation from the sample. Calcium, strontium, and barium were purchased from Mitsuwa Chemical Company and were of nominal purity 99%, whereas magnesium of purity 99.9% was used. The sample was put into a specially deviced cell of 18/8 stainless steel in an argon filled glove box. The X-rays emerged through a beryllium window (0.10 mm) protected by a thin stainless steel sheet (0.01 mm) from attack by the molten sample. This type of cell has been frequently reported[6, 7]. The temperature was measured by a Pt-Pt, 13% Rh thermocouple which was inserted into a hole in the side of the cell. The sample maintained the desired temperature within ±5 deg.

3. Analysis of Intensity Patterns

The observed intensity was corrected by the usual procedures[4, 8] for lost counts, background, absorption and polarization, and analysed as described in the previous papers[4, 5]. The distribution of atoms as a function of the distance r from a given reference atom is obtained from the X-ray intensity $I(Q)$ scattered coherently by N atoms with an atomic scattering factor $f(Q)$ by the well-known relations

$$4\pi r^2 \varrho_0 g(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)\,dQ \qquad (1)$$

and

$$S(Q) = I(Q)/[N f^2(Q)] , \qquad (2)$$

where ϱ_0 is the average number density of atoms, $g(r)$ the pair correlation function, $S(Q)$ the structure factor, $Q = 4\pi\sin\theta/\lambda$, 2θ the angle between the incident and diffracted X-rays and λ the wavelength. In order to convert the observed intensities into electron units, the generalized Krogh-Moe-Norman method[8, 9] was used with the atomic scattering factor calculated by Cromer and Waber[10] including the anomalous dispersion correction[11]. The observed intensities at small Q (less than 0.60 Å^{-1}) have been

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smoothly extrapolated to the value at $Q=0$ making use of the value of $S(0)$ given by the relation

$$\lim_{Q\to 0} S(Q) = S(0) = \varrho_0 \chi_T k T \qquad (3)$$

where k is the Boltzmann constant, χ_T the isothermal compressibility and T the absolute temperature. We used the isothermal compressibilities reported by McAlister, Crozier and Cochran[12]. On the other hand, the Fourier transform of Eq. (1) has been truncated at $Q = 12.0\,\text{Å}^{-1}$. As shown in previous papers[4, 8, 9] the effect of this extrapolation and truncation on the radial distribution function is quite small. The numerical calculation was performed on the NEAC-2200, Model-700, Computer Centre, Tohoku University.

4. Structure Factor and Atomic Radial Distribution Function

Figure 1 shows the structure factor $S(Q)$ for molten magnesium at 680, 790, and 880° C and Fig. 2 shows the structure factors for molten calcium, strontium, and barium near the melting point. As shown in the case of barium in this figure, the structure factor of these three metals is temperature insensitive within the observed temperature region. The positions of the first two maxima of the structure factor are given in Table 1.

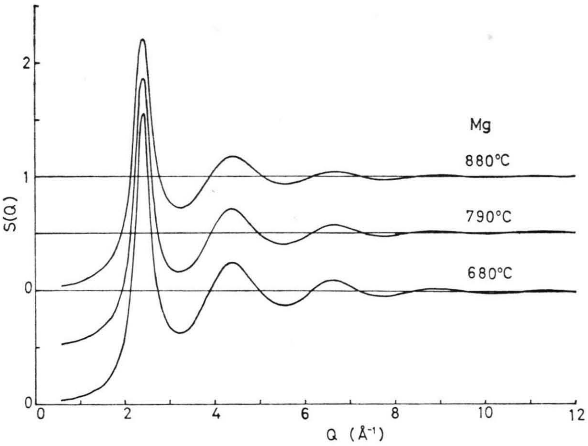

Fig. 1. Structure factor $S(Q)$ of molten magnesium.

The $S(Q)$ curve for molten magnesium at 680° C is close to the previous X-ray result at 675° C of Woerner, Steeb and Hezel[6]. The temperature dependence of the structure factor of molten magnesium has not been studied before. From Figs. 1 and 2, it is clear that the first peak of the structure factor is quite symmetrical and that there is no evidence of a subsidiary maximum. The ratio (Q_2/Q_1) of the positions of the second and first maximum is almost constant ($\cong 1.85$) (see Table 1) and nearly equal to the value ($\cong 1.83$) found for molten alkali metals. The structure factors of molten alkaline earth metals thus look similar to those of the most simple metals such as the alkali metals, in contrast to molten tin, bismuth, and others, which show a subsidiary maximum on the high angle side of the first peak[5]. It is well known that this general form of the structure factor at temperatures just above the melting point agrees with that of the hard sphere model[13] with packing density $\eta = 0.45$, within the first approximation. This model structure factor depends only on the packing density, which is interpreted as the ratio of the total volume of liquid to the volume occupied by the atoms. The former quantity is given by $v_0 = 1/\varrho_0$ and the latter by $v_a = \pi\sigma^3/6$ where σ is the effective hard sphere diameter. Furukawa[14] suggested to put $\sigma = r_1/1.145$ for most molten metals, where r_1 is the nearest interatomic distance directly obtained from experimental data. His suggestion is a good approximation for simple molten metals such as elements having symmetrical peaks of the structure factor. According to his suggestion, the values of σ are 2.80 Å for magnesium, 3.35 Å for calcium, 3.69 Å for strontium, and 3.76 Å for barium. Using

	Temp. (°C)	Density (g/cm³)	Peak positions (Å⁻¹) Q_1	Q_2	Q_2/Q_1	r_1 (Å)	n_1 (atoms)
Mg	680	1.545	2.42	4.40	1.82	3.21	10.9
	790	1.433	2.42	4.40	1.82	3.21	11.0
	880	1.339	2.41	4.40	1.83	3.20	10.8
Ca	850	1.37	1.95	3.62	1.85	3.83	11.1
	890	1.35	1.95	3.62	1.85	3.83	11.2
Sr	780	2.38	1.78	3.30	1.85	4.23	11.1
	830	2.36	1.78	3.30	1.85	4.23	11.3
Ba	730	3.32	1.73	3.21	1.86	4.31	10.8
	780	3.30	1.73	3.21	1.86	4.30	10.6

Table 1. Peak positions, interatomic distance r_1 and coordination number n_1 for molten alkaline earth metals.

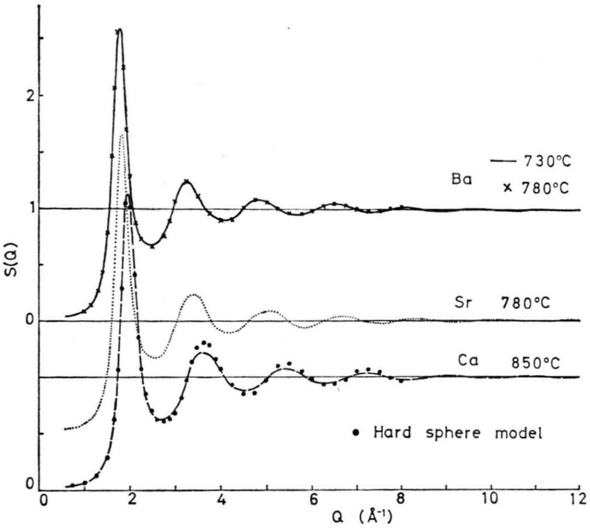

Fig. 2. Structure $S(Q)$ of molten calcium, strontium, and barium.

these values, the packing density $\eta = v_a/v_0$ is 0.42 ± 0.02. On the other hand, the value of $S(0)$ given in Eq. (3) is connected with the packing density in the following way:

$$S(0) = \varrho_0 \chi_T k T = \frac{(1-\eta)^4}{(1+2\eta)^2} \, . \tag{4}$$

The packing density evaluated from this equation with χ_T given by McAlister, Crozier and Cochran [12] is also 0.42 ± 0.03. Both values are close to the value 0.45 proposed for the structure factor near the melting point by Ashcroft and Lekner [13]. As an example a comparison between the experimental data and the model calculation is made in the case of molten calcium at 850 °C. The solid dots in Fig. 2 show the values calculated for the hard sphere model with the packing density 0.45. The method of numerical calculation was identical to the one described in the original work of Ashcroft and Lekner [13]. This comparison shows that the structure factor of molten alkaline earth metals follows that a hard sphere fluid, though it's oscillation is damped more rapidly than that obtained for the hard sphere model. Such a rapid damping is very common in molten metals [15] and often considered to be due to the soft repulsive core in the effective interionic potential of molten metals [16].

As shown in Figs. 1 and 2, the structure factors for the molten alkaline earth metals are insensitive to temperature within the observed temperature region, and in this respect it seems that molten alkaline earth metals are rather similar to the molten II-b divalent metals, zinc [17], cadmium [18], and mercury [19].

Figures 3 and 4 show the pair distribution function $g(r)$ calculated from the structure factor with the density taken from [20–23]. The interatomic distance r_1 and the coordination number of nearest neighbour atoms n_1 evaluated from the atomic radial distribution function, $4\pi r^2 \varrho_0 g(r)$, are listed in Table 1. As there is no unique method for the evaluation of the coordination number [8, 9], only a mean value obtained by three methods [24] is given in this table. The values r_1 and n_1 for molten magnesium at 680° C found in this work are in good agreement with those reported previously [6].

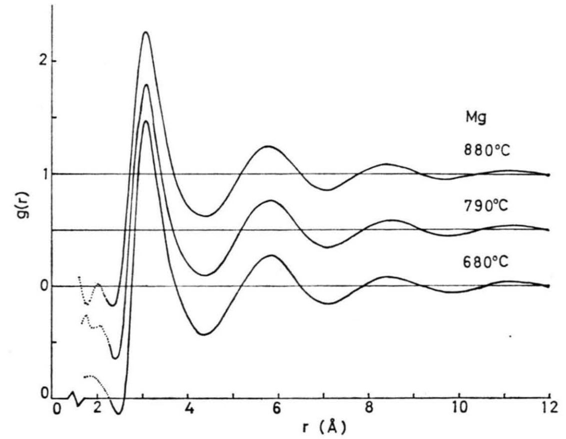

Fig. 3. Pair correlation function $g(r)$ of molten magnesium.

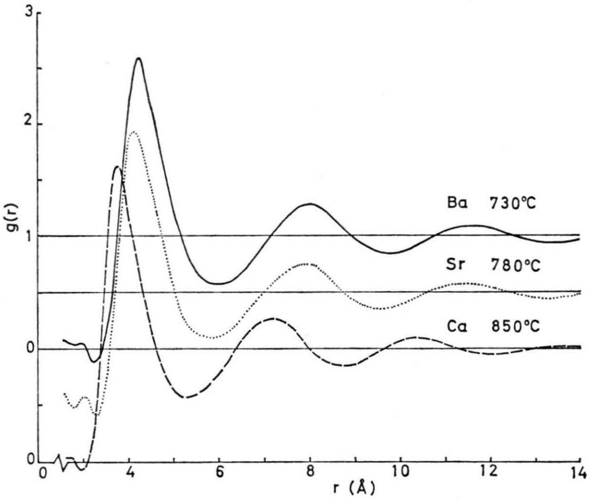

Fig. 4. Pair correlation function $g(r)$ of molten calcium, strontium, and barium.

5. Application to Electron-transport Properties

Using the structural information given in the previous section, we can discuss quantitatively the various properties of molten alkaline earth metals. In this section we present an application of the measured structural information on the calculation of the electrical resistivity and thermoelectric power for molten calcium, strontium and barium at their melting points using Ziman's theory [25].

In the case of molten magnesium, the calculation based on the measured structure factor [6] and the appropriate pseudopotential parameters [3, 13] has already been carried out. Reasonable agreement between experiment and calculation has been reported. In fact, using the pseudopotential parameters of Animalu and Heine [26] the structure factor of molten magnesium at 680° C obtained in this work predicts a value of 21.3 $\mu\Omega$ cm for the electrical resistivity which is in good agreement with the experimental value (26.1 $\mu\Omega$ cm) [2]. Calculations of Van Zytveld, Enderby and Collings [2] for molten calcium, strontium and barium gave values of the electrical resistivity which are smaller than 20 $\mu\Omega$ cm. Ratti and Evans [27] recently reported a calculation on this problem based on the t-matrix of a muffin-tin potential and found good agreement with the experimental data. In their calculation, however, they used the hard sphere structure factor and the muffin-tin potential of an expanded solid with the lattice spacing extrapolated to the density in the molten state. In order to improve the attempt of Ratti and Evans [27] we re-calculated the electrical resistivity and thermoelectric power using the structural information obtained in this work.

The muffin-tin potential in the molten state used in our calculation was constructed from the pair distribution function directly obtained by X-ray diffraction according to the formula proposed by Kukhopadhyay, Jain and Ratti [28]. The method of numerical calculation was identical to the one described in the original papers of Ziman [25] and Ratti and Evans [27]. Figure 5 shows the phase shifts obtained for molten calcium, strontium and barium. The general form of the energy dependence of the d-phase shift obtained in this work is similar to that of Ratti and Evans. But their change of the d-phase shift is rather gentle compared with that calculated from our muffin-tin potential based on the measured information. In Table 2 we list the values of the phase shifts at the Fermi energy E_f to estimate the t matrix and some relevant data. Ω_0 is the atomic volume, E_b is the energy of the bottom of the band measured from the muffin-tin zero and m^* is the effective mass. These values are estimated using the method suggested by Dreirach [29]. On progressing down the periodic table from calcium to barium, all three phase shifts increase in magnitude but the increase in the d-phase shift plays a significant effect on the scattering amplitude as shown in Fig. 5. This implies that the effect of the empty d-states above the Fermi energy in these molten metals which are precursors of the transition series begins to affect the electron-ion scattering processes. The results of the present calculation are given in Table 3 together with those of Ratti and Evans [27] and experimental data [2, 3]. It is evident that a good agreement is found

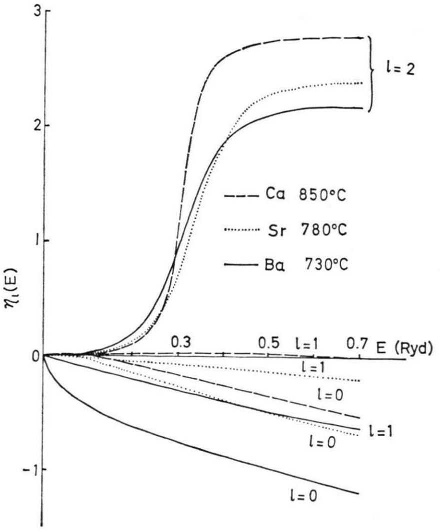

Fig. 5. Energy dependence of the phase shifts for molten calcium, strontium, and barium. The parameter l denotes the angular momentum.

	Temp. (°C)	Ω_0 (a. u.)	E_b (Ryd)	E_f (Ryd)	m^*/m	η_0	η_1	η_2
Ca	850	329.4	−0.019	0.230	1.275	−0.097	0.018	0.191
Sr	780	413.3	−0.007	0.220	1.205	−0.175	−0.045	0.197
Ba	730	463.0	0.027	0.222	1.302	−0.641	−0.224	0.295

Table 2. Phase shifts at Fermi energy E_f for molten calcium, strontium and barium.

	Temp. (°C)	ϱ_{el} ($\mu\Omega$cm) calculation			X calculation		
		Ratti-Evans[27]	present	exp.[2]	Ratti-Evans[27]	present	exp.[3]
Ca	850	28	64	33	−5.6	−3.3	−1.6
Sr	780	66	82	85	−3.3	−1.0	0.06
Ba	730	415	290	306	−1.6	0.8	0.03

Table 3. Comparison of calculated electrical resistivity ϱ_{el} and thermoelectrci power parameter X with experimental data for molten calcium, strontium, and barium.

between the present calculation and the experiments and that the results obtained in this work generally support those in the previous calculation of Ratti and Evans[27]. A large value of the electrical resistivity of molten barium, which is more than several times that of usual molten metals, is also well explained by the Ziman theory of the *t*-matrix formulation so long as we introduce straightly the structural information obtained by diffraction experiments.

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