Reports of the Academy of Sciences of the USSR

A. V. ROMANOVA, B. A. MELNIK

1969

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1969, Volume 189, No. 2

PHYSICS

A. V. ROMANOVA, B. A. MELNIK

X-RAY STUDY OF THE STRUCTURE OF LIQUID LEAD

(Presented by Academician G. V. Kurdyumov, 14 IV 1969)

The structure of various molten metals has repeatedly been investigated by diffraction methods, using experimental techniques of varying degrees of refinement. The results of these studies have been published in numerous original and review articles ($^{1-4}$). In a number of cases, for the same metals, short-range-order parameters have been obtained that differ substantially from one another. The source of this discrepancy apparently lies in the intensity curves—the accuracy of the intensity measurements, the methods of processing, and so forth (^{5,6}).

In the present work an attempt has been made to obtain new information on the structure of liquid lead and its variation with temperature, based on intensity curves obtained with a high degree of accuracy. It should be noted that the intensity curve is the primary source of information on the structure of a liquid; it may reveal details that are not visible in the radial distribution functions of atoms $4\pi r^2\rho(r)$, obtained by Fourier analysis of the intensity curve. For example, for liquid gallium we found on the intensity curve in copper radiation (wavelength $\lambda = 1.54$ Å) a splitting of the principal intensity maximum into two, each of which corresponds to a definite type of grouping of atoms with its “own” short-range-order structure.

The technique used in the work was characterized by the large dispersion ($\lambda = 1.54$ Å), high sensitivity and resolving power of the scintillation crystal and the CCD-type electronic counting apparatus, good stabilization of the operating regime of the x-ray tube and electronic counting apparatus, and monochromatization of the primary beam by means of a perfect germanium single crystal. The illuminated flat surface of the specimen, at a constant beam inclination angle $\alpha = 11^\circ$, had the form of a rectangle measuring 1.6×2 mm. The maximum divergence was small and in the region of the first intensity maximum amounted to $\sim 1^\circ$. The temperature of the specimen was monitored with a thermocouple to an accuracy of $\pm 1^\circ$; the level of the specimen in the center of the camera was maintained by means of a microscope and a special device to within ±0.025 mm. The intensity measurements were carried out at angular intervals of $15'$—$30'$ in the region of the first maximum and $30'$—1° at larger scattering angles. For each temperature several intensity curves with very good reproducibility were obtained and averaged. Thus, the average error in measuring the intensity on the "tail" of the curve was 1%.

Corrections for absorption and polarization were introduced, and refined values of the atomic factors f^2 were used (⁷). The incoherent scattering was small and was not taken into account. The functions $4\pi r^2\rho(r)$ were calculated on the "Mir" electronic computer; in the calculation, intensity values were taken at intervals of 0.5—1° in scattering angle.

The intensity curves of liquid lead at different temperatures (Fig. 1) are characterized by a complex structure of intensity maxima. In contrast to the literature data ($^{1-3,5}$), a very clear splitting of the principal intensity maximum into two is observed, which becomes smoothed out

as the temperature is raised. If the positions of these maxima are compared with the positions of the lines from the crystalline powder (vertical segments in Fig. 1), it turns out that the (111) and (200) reflections correspond to these separately existing diffuse intensity maxima. The further distribution of intensity in the region of the third maximum also reproduces well the pattern of the arrangement of the lines of the crystalline powder (Pb has an f.c.c. lattice with parameter $a = 4.95$ Å). With increasing temperature, the details in the region of this maximum disappear noticeably.

Weak resolution of the most intense maximum of liquid lead was observed in neutron diffraction at a temperature of 330° (^{8}). However

[Figure 1 and Figure 2]

Fig. 1. Intensity curves of liquid lead at temperatures of 340; 385; 400 and 440°

Fig. 2. Radial distribution functions of atoms in liquid lead at temperatures of 340; 385; 400 and 440°

the number of recorded pulses was so small (260-300) that the authors did not succeed in detecting this effect clearly.

Such a diffraction pattern naturally makes it possible to speak of the presence in the melt of groupings of atoms of considerable size with short-range order corresponding to the solid phase.

Using the good resolution of the intensity maxima and the expression (^{9}): $\Delta S = 1.58 \cdot 2\pi h^2/R$, where $S = 4\pi \sin\theta/\lambda$; ΔS is the integral width of the maximum; R is the radius of the ordered region; h is the order of the maximum, we find that at a temperature of 340° R may be from 26 to 30 Å. (The values of R were determined, respectively, from the widths of the first and second maxima.)

The possible influence on the scattered intensity of PbO oxide, which may form at the temperatures under investigation ([10,11]), was checked. The positions of the oxide lines and of the intensity maxima differ strongly.

The radial distribution functions of atoms (Fig. 2) made it possible to determine the parameters of short-range order—the most probable interatomic distance r_1 and the mean coordination number n_1 (obtained by extending the right-hand branch of the first maximum to its intersection with the distance axis r). At temperatures of 340–400°, n_1 is close to the coordination number of the crystalline lattice, and only at 440° is it noticeably lower (see Table 1). This is in good agreement with the data ([1–4]) for tempera-

temperatures close to the melting point. In work ([5]) the coordination numbers are not given. The interatomic distance r_1 is somewhat smaller than the radius of the first coordination sphere of solid lead ($r = 3.49$ Å). A decrease in r_1 after melting was observed in ([2],[3],[5]); in a number of other works r_1, unfortunately, is not given.

As can be seen from Fig. 2, the atomic distribution functions are not free of false maxima caused by the truncation effect of the intensity curve. However, we did not introduce corrections for this effect in the manner of ([5]), since the false maxima are small and symmetric in shape. The accuracy of the intensity curves and $S_{\max} = 7.4\ \text{Å}^{-1}$ proved sufficient to obtain r_1 in agreement with ([5]), where such corrections

Table 1

T-ra, °C	I	II	III	IV	$S_{\max}$	n_1	r_1
340	2.21	2.52	4.11	5.46–6.51	7.4	10.8	3.45
385	2.21	2.52	4.11	5.46–6.51	7.4	10.8	3.40
400	2.21	2.52	4.08	5.67–6.51	7.4	10.7	3.40
440	2.21	2.50	4.03	5.67–6.60	7.4	10.3	3.39

were carried out. In analyzing the entire distribution curve, which is omitted here, the positions of the false maxima were taken into account according to ([6]).

Thus, in the interval 340–440° for four temperatures, data were obtained on the short-range-order parameters of liquid lead, and an estimate of the regions of ordering was made from the intensity curves.

If one calculates the atomic density, knowing n_1 and r_1, for solid and liquid lead, one obtains values respectively of 0.020 atoms/Å^3 and 0.021 atoms/Å^3, differing little from one another, which contradicts the increase in the volume of lead upon melting.

Consequently, such experimental facts as the splitting into two of the principal intensity maximum, the decrease in interatomic distance and coordination number in comparison with the solid phase, and the increase in volume after melting while the microscopic density of atoms is retained can be successfully explained if one imagines the following picture of the structure of liquid lead. There are ordered regions of large size, in which the packing of atoms is of the same type as in the crystal lattice, but with a somewhat smaller distance. Between these regions local gaps are formed, owing to which the volume of lead increases upon melting. Raising the temperature leads to a decrease in the size of these regions while preserving the type of packing, which is reflected in a lowering of the coordination number and in the blurring of the splitting of the principal intensity maximum.

Institute of Metal Physics
Academy of Sciences of the Ukrainian SSR
Kiev

Received
9 IV 1969

REFERENCES

1. V. I. Danilov, *Structure and Crystallization of Liquids*, Kiev, 1956.
2. I. V. Radchenko, UFN, 61, no. 2, 249 (1957).
3. A. F. Skryshevskii, *X-ray Diffraction of Liquids*, Kiev, 1966, p. 59.
4. Ya. I. Dutcha , A. G. Mykolaichuk, N. T. Klym, FMM, 14, no. 4, 548 (1966).
5. R. Kaplow, S. L. Strong, B. L. Averbach, Phys. Rev., 138, 5A, 1366 (1965).
6. R. Hosemann, K. Lemm, H. Krebs, Zs. Phys. Chem., 41, H. 3/4, 121 (1964).
7. B. D. T. Kramer, J. T. Weber, Acta crystallogr., 18, 104 (1965).
8. B. I. Khrushchev, A. M. Bogomolov, L. S. Sharapova, FMM, 22, no. 2, 279 (1966).
9. B. K. Vainshtein, *Diffraction of X-rays by Chain Molecules*, Acad. Sci. USSR Press, 1963.
10. O. Kubaschewski, B. Hopkins, *Oxidation of Metals and Alloys*, 1955, p. 254.
11. J. Benard, *Oxidation of Metals*, 1, IL, 1968.

Note: Figure translations are in progress. See original paper for figures.