The short-range order in the surface layers of Cu-Au (Ge) melts by electron diffraction

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Abstract. An apparatus for measurement of electron beam diffraction from the surface of a melted droplet is described. The basic features of the method are discussed. The main results for the binary melts are presented. An effective algorithm is proposed to determine the cylindrical distribution function of the atoms in the melt surface by diffraction experiment data.

1. Introduction
In the last years, experimental methods capable to provide direct information about the short-range order of the interface boundary have been developed. Among them the diffraction methods can open the short-range order in the surface layers.

Intensive interaction of electrons with the substance of a sample permits reduction of the time of exposures down to 5-10 seconds, which decreases pollution of the surface with components of gas phase and material of a container and is rather substantial in high temperature experiments. A well-focused beam of electrons with low radiation under small angles of dropping can be received in serial electron microscopes. Let us present experimental and theoretical peculiarities of the method.

2. The apparatus and experimental procedure
For realization of the method, a special apparatus was used [1] in which the electron beam in a microscope with a vertical axis could interact under a glancing angle with a melt surface.

A cell was designed for implementation of the method. The cell provided melting of the metal, placing it together with the furnace in the microscope column, and obtaining a diffraction pattern of the electron beam scattered by the surface.

As soon as the sample was molten and the furnace was turned off, a focused beam of electrons was directed to the droplet edge at a slow cooling (~1 K/s) and emergence of extended smeared fringes was observed on the fluorescent screen of the microscope. While cooling the system, the intensity of the fringes changed and the most complete spectrum of lines was stabilized at a temperature of about 100 degrees before crystallization. Then the spectrum lines disappeared.

The presence of long smeared rods in the electron diffraction pattern testifies to a two dimensional diffraction from surface layers of the droplet and also to a "monatomic" smoothness of the liquid surface. So, the diffraction pattern contains information about two- and three atom layers of the melt.
An analysis of the obtained electron diffraction patterns revealed the presence of doublets and shifts of the fringes relative to each other.

**Figure 1.** The influence of the electron penetration depth on the shift of diffuse lines (the arrow marks the reflex shift).

Such splitting was noted in literature. Using the shift of fringes, the intensity of radiation scattering only from the surface layer of atoms was measured. It was of interest to obtain information about both the structure of the surface layer and the distribution of atoms in subsequent layers within a single experiment. Therefore the depth component of the structure factor was separated. Peaks of scattering from deep layers and the surface layer were identified basing on the shift. Then, comparing relative heights of the composite peaks in the doublets of the total structure factor we determined the contribution of each layer to scattering. Afterwards, the structure factors for the second layer and the subsequent layers were found.

In the case of a two dimensional isotropic medium a cylindrically symmetric distribution of intensity corresponds to a cylindrical symmetry of atom distribution in the surface.

### 3. Calculation procedure

The direct transform, which is usually made to extract the information about distribution of the scattering centers using the sine Fourier transform is incorrect in case of surface layer, because the Zernicke-Prince equation is derived in proposition of remoteness of the central atom from the interface.

Assuming the part of the drop surface interacting with the radiation as the two-dimensional isotropic medium, the following equation is obtained for the cylindrical distribution function [1,2]:

\[
2\pi \rho^o (r) = 2\pi \rho_0^o + \int_0^\infty s \left[ a^o (s)-1 \right] J_0(sr) \, ds , \quad \rho_0^o = -\frac{1}{2\pi} \int_0^\infty s \left[ a^o (s)-1 \right] ds \quad (1)
\]

where \( J_0(sr) \) is zero order Bessel function of the first kind, \( \rho_0^o \) is average surface density. For the equations (1) tear effect arises. It is caused by limitation of the experimental information about \( a^o (s) \) on the finite interval \( (s_{min}, s_{max}) \). To reduce it, integral equation of the first kind with fixed borders is usually solved by regularization methods. Nevertheless this approach does not take into account the properties of the Fourier transform on the half-line.

If we apply inverse Fourier-Bessel transform and denote \( f(s) = \left[ a^o (s)-1 \right] : 2^{1/2} \), then

\[
f(s)(2s)^{1/2} = \int_0^\infty 2\pi r^{1/2} \left[ \rho^o (r) - \rho_0^o \right] (sr)^{1/2} J_0(sr) \, dr . \quad (2)
\]
To calculate the $\rho^w(r)$ function, consider an algorithm of the equation (2) solution based on the expansion of the $f(s^{1/2})$ function into the series by orthonormal Laguerre functions. Laguerre functions for $n = 0, 1, ..., n$ are given by the recurrent formula:

$$
\Psi_n(x) = e^{-x/2}L_n(x), \quad L_{n+1}(x) = -[L_n(x)(x-2n-1) + L_{n-1}(x)n]/(n+1), \quad L_0(x) = 1, \quad L_1(x) = 1-x.
$$

After change of variables, Laguerre functions become characteristic functions of Fourier-Bessel transform:

$$
\int_0^\infty \varphi_n(r) J_0(sr)(sr)^{1/2} \, dr = (-1)^n \varphi_n(s), \quad \varphi_n(r) = (2r)^{1/2} e^{-r^2/2} L_n\left(r^2\right).
$$

The solution $\rho^w(r)$ looks like $\rho^w(r) = \rho^w_0 + (2\pi r)^{-1/2} \sum_{k=0}^\infty (-1)^k \alpha_k \varphi_k(r)$, where

$$
\left(a^w(s)-1\right)s^{1/2} = \sum_{k=0}^\infty \alpha_k \varphi_k(s), \quad \alpha_i = \int_0^\infty f(s) \varphi_i(s) \, ds = \int_0^\infty f(s^{1/2}) \Psi_i(s) \, ds.
$$

Thus, in case of exact information about $a^w(s)$ on $(0, \infty)$, it is possible to determine coefficients $\alpha_i$ for $f(s^{1/2})$ from the equation (3) and then calculate $\rho^w(r)$ for any $r$. If $a^w(s)$ is measured on the interval $(0, s_{\text{max}})$, we have to change limit $\infty$ to $s_{\text{max}}$ in the integrals (4) to calculate $\alpha_i$. Results of the calculation are presented in Table 1.

| Composition       | $\rho^w_0$, nm$^{-2}$ | $Z^w_1$ | $r^w_1$ |
|-------------------|-----------------------|---------|---------|
| Cu                | 40.7                  | 9.3     | 2.46    |
| Cu 80% Au 20%     | 15.4                  | 4.5     | 2.67    |
| Cu 44% Au 56%     | 15.4                  | 5.7     | 2.67    |
| Cu 20% Au 80%     | 15.4                  | 3.0     | 2.57    |
| Au                | 27.9                  | 7.6     | 2.55    |
| Ge                | 35.8                  | 8.0     | 2.67    |

We have also designed a method to accelerate this calculation. It is based on Gauss-Laguerre quadrature formula that is analogous to Fast Hermite projection method [3]. The acceleration of calculation is close to 10 times with good accuracy.

4. Diffraction results and discussion

As it was shown above the interference function of a two dimensional isotropic medium is related to the atomic distribution function by the Fourier-Bessel expression. The main results for pure gold, copper and germanium have been presented in [2] and for binary melts - in the Table 2.

The structure factors of copper-gold melts, which characterize scattering on surface layers for the entire interval of concentrations studied, is of the form inherent in structure factors of dense metals, i.e. they do not have collateral peaks. S-coordinates of their peaks change almost linearly with the concentration (Table 2). An analysis of the peaks of the $D(r)$ curves has showed that a close packing
with a statistical distribution of atoms of different species is realized in the surface of the melts. The first peaks of the difference functions of cylindrical atomic distribution in the surface and subsequent layers are composite. They cover atomic distances formed by atomic pairs (Cu-Cu, Cu-Au and Au-Au). While the copper concentration in the melt increases, the curve peaks are shifted smoothly, almost linearly, towards smaller distances. The distances, which are characteristic of a mean statistical distribution of atoms in the melt \(r_i/r_1=1.0, 1.83, 2.64, 3.45, \ldots\), are found under the peaks of the difference function of atomic distribution in the surface and deeper layers.

| Table 2. Short-range order parameters of the surface of Cu-Au and Cu-Ge alloys. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Layer          | Composition   | I-1 | I-2 | II-1 | II-2 | III |
|-----------------|---------------|-----|-----|------|------|-----|
| Surface         | Cu 80% Au 20% | No prepeak | 28.7 | 61.0 | 83.0 |
|                 | Cu 44% Au 56% | "---"    | 27.5 | 59.0 | 82.0 |
|                 | Cu 20% Au 80% | "---"    | 26.5 | 57.0 | 81.0 |
| Volume          | Cu 80% Au 20% | No prepeak | 26.6 | 49.0 | 53.0 | 76.0 |
|                 | Cu 44% Au 56% | "---"    | 26.6 | 48.0 | 53.0 | 75.0 |
|                 | Cu 20% Au 80% | "---"    | 26.6 | 48.0 | 53.0 | 75.0 |
| Surface         | Cu 80% Ge 20% | 22-23 | 28.7 | 59.0 | 63.9 | 84.5 |
|                 | Cu 36% Ge 64% | 22-23 | 28.0 | 58.0 | 62.0 | 84.0 |
|                 | Cu 20% Ge 80% | 22-23 | 27.7 | 55.0 | 60.0 | 82.0 |
| Volume          | Cu 80% Ge 20% | 21-23 | 25.5 | 48.0 | 52.0 | 78.0 |
|                 | Cu 36% Ge 64% | 21-23 | 25.5 | 48.0 | 52.0 | 77.0 |
|                 | Cu 20% Ge 80% | 21-23 | 24.5 | 48.0 | 52.0 | 76.0 |

In the Cu-Ge system the first of the chosen compositions \((\text{Cu}_{80}\text{Ge}_{20})\) is close, judging by the equilibrium diagram of a quasi-eutectic type, to the chemical compound \(\text{Cu}_3\text{Ge}\), the second one composition \((\text{Cu}_{64}\text{Ge}_{36})\) corresponds to the eutectic, and the third composition \((\text{Cu}_{20}\text{Ge}_{80})\) is found in the hypereutectic region.

The equilibrium diagram of the Cu-Au system has a cigar-like form degenerating to the eutectic. Here the hypoeutectic \((\text{Cu}_{80}\text{Au}_{20})\), eutectic \((\text{Cu}_{44}\text{Au}_{56})\) and hypereutectic \((\text{Cu}_{20}\text{Au}_{80})\) compositions were examined.

In the Cu-Ge system with 20 mol % germanium in the melt volume a collateral peak is observed on the main peak of the surface structure factor on the side of small angles and splitting of the second peak is noted. As the germanium concentration is raised, the height of the pre-peak increases and splitting of the second peak persists. This behavior is typical for \(a(s)\) of deeper layers, a fact which is due to germanium microgroups appearance, along with the \(\text{Cu}_3\text{Ge}\) compound, in the near-surface layers. The microgroups of germanium appear as a result of its capillary activity in Cu-Ge alloys. With an increase in the germanium concentration, the \(s\)-coordinate of the first peak \(a(s)\) in the surface decreases gradually as the center of gravity of the peak is shifted owing to a rise in the fraction of microgroups of germanium atoms. Even at 80 mol % Ge one can talk about filling of the surface predominantly with germanium.

As in pure metals, the first peaks of difference function \(D(r) = 2\pi[r \rho_0(r) - \rho_i(r)]\) are shifted to the region of shorter distances compared to the bulk melt (Table 2).

Two shortest distances were determined from positions of peaks of the difference distribution function in the surface of the liquid alloy at 20 mol % germanium: \(r_i\), which is close to parameter \(a = 0.264\) nm of the hexagonal lattice of the \(\text{Cu}_3\text{Ge}\) compound, and \(r_i'\), which is the first shortest distance in the surface of liquid germanium.

This set of distances is preserved in the surface at 36 mol % Ge too. And only at 80 mol % germanium the distances characteristic of the microgroups of the compound were not detected on the \(D(r)\) curve of the surface monolayer. They are preserved only on the difference function.
corresponding to subsequent layers. Probably, the entire surface is already filled with germanium atoms.

**References**

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