Resistivity of Cu, Ni and Sb in undercooled liquid state

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Abstract: With the help of non-contact measurement, electrical resistivity of Cu, Ni, Sb has been measured to study the influence of short range order on electrons scattering in the normal and undercooled liquid state. Till the maximum undercooling, linear resistivity-temperature dependence is obtained in Cu and Ni melts. Nonlinear resistivity behavior is obtained in undercooled liquid Sb till a maximum undercooling of about 60 degree. The increase in viscous flow activation energy reveals structure transition in Sb melts. A drop in resistivity of Cu melts is obtained accompanying the recalescence. The abrupt jump in resistivity of Sb reveals the rapid growth of Peierls distortion during rapid solidification process.

1. Introduction
Undercooled melts have been drawing a lot of technological and scientific interest, such as metastable phase fabrication [1], exploring solidification process [2] and structure transition [3]. Recently, the icosahedral short range order (ISRO) hypothesized by Frank [4] to understand the nucleation barriers is verified [5]. It is also found that the distortion of ISRO caused by the atomic interaction is dominated by the electron state and electron interaction [6], which stables the metastable undercooled melts. More and more proofs show that, ordered structures are deduced to exist in liquid and undercooled semimetals [7], such as Peierls distortion including covalent bonds, which results in the attractive behavior of thermo-physical properties. These results make the electron scattering behavior very interesting in undercooled liquid state.

In a sense, rapid solidification process is also the structure transition process including ordered clusters in undercooled melts. Icosahedral clusters plays an important role in the structure transition of metastable phases [8], such as lowering the interfacial energy and nucleation barriers in the rapid solidification of icosahedral quasicrystals [9]. Peierls distortion is also believed to be important in solidification process of semimetals, in terms of structural relationship between liquid and solid states [7]. Electrons scattering behavior draw a lot of scientific interest for high sensitivity to structure transition of undercooled melts [3]. However, very few works have been reported to clarify the impact of structure evolution on electron scattering in undercooled metallic melts, not to say during the rapid solidification process. In this paper, with the help of non-contact measurement, resistivity of Cu, Ni, Sb has been measured to probe the evolution of short range order and its impact on electron scattering.
in undercooled state, as well as subsequent rapid solidification process. Viscosities of liquid Cu and Sb are also measured to characterize the evolution of local clusters during cooling process.

2. Material and methods
The resistivity measurements were performed from superheated liquid to the rapid solidification process in self-constructed equipment. In the apparatus, the samples are placed in a secondary coil (test coil) that is connected in series with a reversely wound identical coil (reference coil). The two secondary coils are placed in a same primary coil that generates an alternating current magnetic field, respectively. A voltage is induced over the test coil by mutual inductance, which is monitored by a differential amplifier. The reference signal is supplied to the differential amplifier with a voltage generated by the alternating current of the primary coil. Theoretically, the differential signal over the secondary coil is zero if there is no sample in the test coil. The coil system with the sample would generate a voltage related to the resistivity of samples.

Then, in a uniform periodic external magnetic field \( H \) with angular frequency \( \omega \), for a cylinder non-ferromagnetic sample with isotropic resistivity \( \rho \), the alternating field \( H_s \) inside the sample can be obtained by Maxwell’s equations based on electromagnetic induction. In terms of effective permeability \( \mu_{\text{eff}} \) proposed by Foster, the alternating field can be expressed as \( H_s = \mu_{\text{eff}} H \), and the effective permeability

\[
\mu_{\text{eff}} = \frac{2}{\sqrt{-i\omega \mu_0 r^2 / \rho}} \frac{J_1(\sqrt{-i\omega \mu_0 r^2 / \rho})}{J_0(\sqrt{-i\omega \mu_0 r^2 / \rho})}
\]

where \( r \) is the radius of the sample and \( \mu_0 \) is the vacuum permeability.

According to Faraday’s law and Kirchhoff’s second law, differential voltage between effective voltage induced in the signal receiving coils and that of the reference coils can be described as

\[
\Delta U = K \left( \left| \mu_{\text{eff}} - \frac{H_{i,0}}{\mu_r} \right| - \frac{\mu_{i,0}}{\mu_r} + \frac{2IS}{l_s S_x} \times \frac{\mu_{i,0}}{\mu_r} \right)
\]

where \( l_s, S_s \) are the length and cross section area of the sample, respectively, \( l, S \) are the length and cross section area of the coils, \( \mu_{i,0}, \mu_r \) are the relative permeability of air and the sample, \( K \) is a parameter dependent on the circuit and working frequency. When the working frequency is fixed during the measurement, then the resistivity can be obtained through the received voltage. Further details of the contactless measurement device could be found in Ref. [13].

Cu(5N), Ni(4N), Sb(4N) about 30g were used in the non-contact measurement of electrical resistivity. The metals were pre-melted in induction furnace under 5N Ar gas. The temperature calibration is made during a simultaneous detection by pyrometer (Raytek 3i) and S-type thermocouple, during the cooling process. The accuracy of temperature is about ±5 K. The metals were undercooled with the help of \( \text{B}_2\text{O}_3 \) flux. The evaluated absolute error in resistivity was no more than 3%, because of the uncertainty in signal fluctuation and temperature error.

Viscosity measurement was performed using an oscillation cup viscometer for high-temperature melts made in Japan. The samples were placed in an alumina crucible hung by a torsional suspension, and heated at a rate of 4 K/min to about 150 K above the melting points; after maintaining those temperatures for 1 h, samples were cooled down to experimental temperatures and held for 20 min prior to each measurement. Dynamic viscosities of melts were calculated by using Shvidkovskiy equation [11, 12]. Viscosity experiments were repeated for three times at each temperature. The data error of different measurements at the same temperature was no more than 3%.

3. Results
Fig. 1 (a) and (b) present the resistivity-temperature behavior of Cu, Ni in undercooled liquid and
subsequent solidification process. During the measurement, the maximum undercooling of ~131 and 208 K was obtained for Cu, Ni, respectively. Obviously, resistivity decreases linearly with decreasing temperature in the melts till the maximum undercooling. It is worthy to notice, there is an obvious drop in resistivity accompanying the recalescence. Then, a temperature plateau is observed where resistivity decreases as solidification processes.

Fig. 1 Resistivity-temperature dependence of Cu (a) and Ni (b) in undercooled liquid state and during subsequent rapid solidification process

Fig. 2 shows the resistivity-temperature behavior of Sb in undercooled liquid and subsequent solidification process. During the cooling process, the resistivity-temperature curve of Sb melts can be divided into two regions. When the temperature is higher than about 1000 K, the resistivity decreases linearly with decreasing temperature. While lower than 1000 K, the resistivity-temperature curve is deflected upwards till the maximum undercooling. The resistivity dependence of temperature could be well fitted as:

\[ \rho = 85.258 + 0.0299T \]  \hspace{1cm} (3)

\[ \rho = 128.691 - 0.0382T + 2.506 \times 10^{-5}T^2 \]  \hspace{1cm} (4)

What’s more, a jump in resistivity is observed accompanied by the recalescence, which is quite different from those of Cu and Ni melts. And then, resistivity increases in the subsequent temperature plateau as solidification process.

Fig. 2 Resistivity-temperature dependence of Sb in undercooled liquid state and during subsequent rapid solidification process
As shown in Fig. 3, viscosity of Cu melts behaviors with temperature following Arrhenius dependence around melting point, with the activation energy of viscous flow ($E_v$) of 1576 J/mol. In Sb melts above 990 K, viscosity-temperature curves can be well fitted following Arrhenius dependence, as shown in Fig. 4. However, as temperature decreases, an obvious inflection with increasing activation energy is observed till the melting point. The $E_v$ after the inflection rapidly increases to 1134 J/mol from 618.4 J/mol.

In normal liquid Cu, Ni and liquid Sb above 1000 K, the atoms and free electrons are randomly arranged. Then, electrical resistivity results from electron-ion interaction. Generally, the resistivity-temperature dependence is determined by the density fluctuation with temperature. Since the density decreases with decreasing temperature, resistivity decreases linearly with decreasing temperature [13, 14], as it is well known.

Resistivity of liquid metals [15] can be understood by Ziman theory:

$$\rho = \frac{3\pi}{4e^2\hbar v_F^2\Omega k_F^4} \int_0^{2k_F} V^2(q)S(q)q^3 dq$$

(5)

where $k_F$ is Fermi wave number, $S(q)$ is structure factor, $q$ is wave number. $V$ is pseudopotential form factor. So, resistivity is determined by the position of $2k_F$, which typically locates near the maximum in the first oscillation for $S(q)$. In normal liquid metals, it is verified that linear resistivity behavior is due to the sharpening of main peak in structure factor, which is responsible for the linearly increasing
density with decreasing temperature.

4. Discussion

4.1 The impact of icosahedral clusters
As Cu and Ni melts come into undercooled liquid state, the existence of icosahedral clusters has been verified in diffraction studies of undercooled liquid Cu and Ni [16,5]. Then, the effect of formation of icosahedral clusters on temperature coefficient of resistivity (TCR) is very interesting. As shown in Fig.1 (a) and (b), the TCRs of Cu and Ni melts keep constant till the maximum undercooling in present research. This implies that the evolution of local clusters in undercooled melts would not influence the TCR, although the percentage of ordered clusters increases with increasing undercooling which is indicated by structure investigation.

In undercooled liquid Cu and Ni, recent studies on local structure demonstrate that, while icosahedral clusters are dominant, a significant numbers of the ordered atoms in icosahedral clusters also sit in other environments, such as BCC and FCC-like structure [17]. These ordered atoms in icosahedral clusters also have the same coordination number with other atoms in undercooled melts. Then, the interaction between free electrons and ions (atoms) in icosahedral clusters is very similar to that of other geometrical ordering. Besides, viscosity results indicate no existence of abnormal change in the size of local clusters, as shown in Fig. 3. On the other hand, icosahedral order, BCC and FCC belong to geometric short-range order, thus the formation of icosahedral clusters will not influence free electron density in undercooled Cu and Ni melts. So, scattering effect caused by formation and increase of icosahedral clusters would not change the linear TCR.

Compared to equilibrium liquids, the main structure characteristics are the existence of icosahedral clusters in undercooled transition and noble metals. The signature (if there is) of icosahedral clusters [5] is believed to be the shoulder at the high-\(q\) side of the second peak in structure factor \(S(q)\), on the assumption of a single dominating icosahedral cluster in the liquid. For metallic melts, the shoulder at the high-\(q\) side of the second peak is much larger than \(2k_F\). Thus, the shoulder [18] in the second peak of \(S(q)\) takes little role in resistivity and TCR following Ziman theory. Then, constant TCR in undercooled liquid Cu and Ni melts could be well interpreted.

4.2 The impact of Peierls distortion
As for Sb melts lower than 1000 K, Sb clusters with Peierls distortion survives [6, 14], in which the covalent bonds would prevent the formation of icosahedral clusters in undercooled Sb melts [19, 20]. The formation of covalent bonds leads to the decrease of electron density in the melts, which weakens the decrease of resistivity with decreasing temperature. Due to the higher structure similarity to the crystalline phase, Sb clusters with Peierls distortion decrease the liquid-solid interfacial energy and will provide preferential nucleation sites in solidification process [21]. As nucleation nuclei, thus the amount and size of Sb clusters with Peierls distortion increases with decreasing temperature, which is consistent with viscosity results in Fig.4. The larger size of Sb clusters means lower free electron density and stronger scattering effect on free electrons. Therefore, the decreasing TCR with increasing undercooling is well interpreted as the overall effect of temperature fluctuation and formation of Sb clusters with Peierls distortion.

4.3 Resistivity in recalescence plateau
It is interesting that, an obvious drop and jump are obtained in the resistivity curves of undercooled liquid Sb and Cu, respectively. The drop in resistivity of Cu is quite similar to that of undercooled liquid Cu-Ni alloys [3]. Around melting point, the resistivity of solid Cu is about one-third as that of liquid Cu. Taking account of the large undercooling, a large fraction of solid phase forms during recalescence process. Thus, it is reasonable to conclude that the rapid drop in resistivity indicates the larger fraction of solid phase with low resistivity.

For Sb melts, the resistivity of solid phase is larger than 160 \(\mu\Omega\cdot\text{cm}\), while the liquid phase is only
about 120 μΩ·cm. Then, the formation of solid phase and the raise of temperature during recalescence contribute to the rapid increase in resistivity. The raise in sample temperature would not be the main reason in the increase of resistivity [3]. On the other hand, taking account of maximum undercooling of 60 K and the large temperature plateau, the fraction of as-solid phase is very low during recalescence process. Then, it is reasonable to conclude that it is the rapid formation of Peierls distortion with covalent bonds rather than high solid phase fraction determines the jump in resistivity. This hints that the growth of Peierls distortion with covalent bonds may be more rapid than that of solid phase in the rapid solidification of undercooled liquid Sb.

5. Conclusion
Constant TCRs are determined by the evolution of local structure in undercooled liquid Cu and Ni. While the resistivity-temperature curve of undercooled Sb melts is inflected upwards due to the enhancement of Peierls distortion with covalent bonds, consistent with the present viscosity results. Accompanied by recalescence, the abrupt drop and jump in resistivity of Cu and Sb are due to the rapid growth of solid phase and Peierls distortion, respectively.

Acknowledgements
We thank the support from Project supported by the National Science Foundation for Youths of China (Grant No. 41806112 and 51802179), National Key Research and Development Plan of China (Grant No. 2018YFF01014101), Project supported by Shandong Province Science Foundation for Youths (Grant No. ZR2018LE005), Key Research and Development Program of Shandong Province (International Science and Technological Cooperation) (Grant No. 2019GHZ005), Major Scientific and Technological Innovation Program of Shandong Province (Grant No. 2019JZZY020302), and Project supported by Excellent Youth Innovation Team of Shandong Province (Grant No. 2019KJA005) , Project (Z135060000070) and (Research and development of integrated technology and equipment for high salinity and high concentration organic wastewater treatment, 2020KJC-ZD13 ).

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