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Investigating the Optical Properties of Mercury (Hg) Nanoparticles Using CryoSTEM-VEELS

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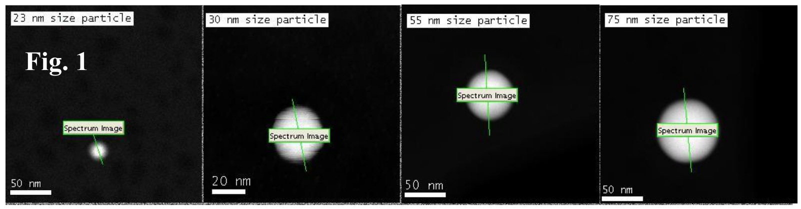
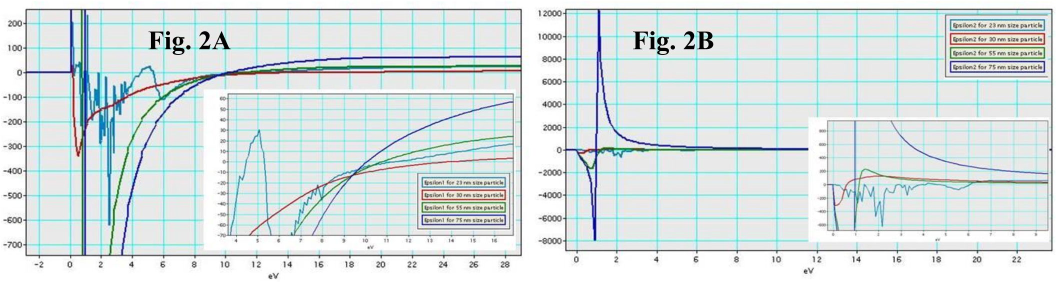
Optical properties of Hg metal had been a topic of discussion in the past due to some discrepancies generated by the predictions of free electron gas (Drude) model and their experimental observations [1, 2, 3]. Little new insights were brought in understanding these properties for both solid and liquid phases of Hg. Hence a renewed effort was attempted in this report to investigate the optical properties of Hg using the technique of scanning transmission electron microscopy and valence electron energy loss (STEM-VEELS). STEM-VEELS spectrum imaging (SI) datasets were acquired from Hg nanoparticles of different sizes sitting on a carbon film at the temperature of 100 K and at the vacuum level below 0.1 mPa. Entire experiments were carried out using a Titan TEM (FEI Company, Hillsboro, OR) operating at 300 kV and equipped with an energy filter (Tridiem GIF from Gatan, Inc.). Furthermore, SI datasets were acquired with 0.7 nm and 1.4 eV spatial and energy resolutions, respectively. Kramers-Kronig (KK) analysis was then applied to single scattering data (SSD) after the plural scattering contribution was first removed. Various optical parameters such as dielectric function ($\boldsymbol{\varepsilon} = \varepsilon_1+\varepsilon_b + i\varepsilon_2$) of Hg nanoparticles in solid phase were determined and discussed as a function of energy loss.

High angle annular dark-field STEM (HAADF-STEM) micrographs of various size nanoparticles are shown in Fig.1. A STEM-EELS SI dataset was acquired along a line across each nanoparticle of Fig.1. Real (ε_1) and imaginary (ε_2) parts of $\boldsymbol{\varepsilon}$ were determined from the central regions (5 nm) of each Hg nanoparticle using the KK analysis (Fig. 2A and Fig. 2B). The bulk Plasmon energy ($E_p=\hbar\omega_p$) is usually determined as the energy loss value at which ε_1 turns zero. According to Drude model, E_p was predicted to be 10.9 eV for Hg metal [1]. However, its exact measurement had always been subject to discussion [1, 2]. Interestingly our observations show that E_p energy of 75 nm and 55 nm size nanoparticles was close to the one predicted by Drude model (Fig.2A). This implies that electronic behavior for these two particles is nearly like a free electron gas. On the other hand, a strong coupling of interband transitions (ε_b) was noticed for 30 nm and 23 nm size nanoparticles. In fact, the effect of these interband transitions was much stronger in the case of 20 nm size nanoparticle as its ε_1 was pushed above zero at ~ 4.5 eV energy loss possibly due to s-d type transitions (Fig. 2A). Whereas for 30 nm size nanoparticle Ep had been blue-shifted to 14 eV energy value but contribution of s-d type transitions at 4.5 eV was found to quite less unlike the 23 nm size particles. Interband transitions occurred quite significantly at the surfaces (3 nm) of all nanoparticles as shown in Fig.3A and Fig. 3B by the multiple oscillations of ε_1 and ε_2 in the range of 2-8 eV energy loss. It can also be noted in Fig. 3 that only 75 nm size particle exhibited the surface plasmon energy of ~6.3 eV as predicted by Drude model [1] and the rest of smaller size nanoparticles showed strong surface effects. Finally the bulk moduli (B_m) could be calculated for these nanoparticles since it is related E_p energy [4]. The value of B_m for 75 nm size nanoparticle turned out to be 41 GPa. This is higher than the already reported value of 25 GPa at the temperature and pressure of 20 °C and 19 MPa, respectively [5]. An apparent difference of ~15 GPa between the two values could be due to having quite different temperature and pressure conditions between the two set experiments namely in the TEM column than in the ref. [5].

In conclusion, STEM-VEELS technique offered the opportunity to revisiting the optical properties of Hg metal at the nanoscale length. Nonetheless a lot more work is still remained to be understood both on experimental and theoretical aspects of EELS data from these Hg nanoparticles.





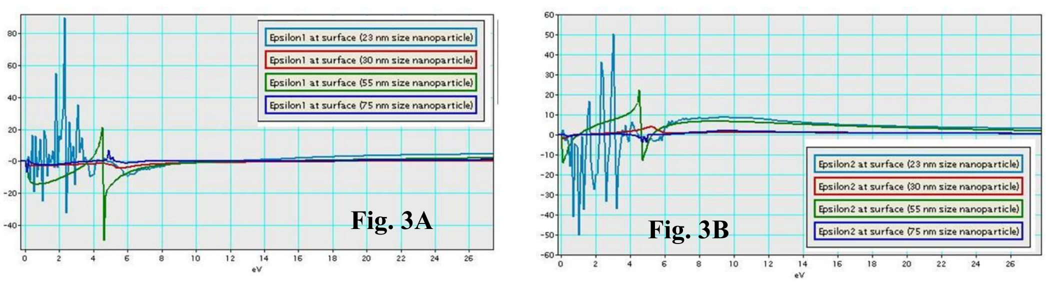


Fig.1: HAADF-STEM micrographs of Hg nanoparticles examined using STEM-VEELS. Each SI dataset was acquired with ~450 $e^-/Å^2$ dose along scan-lines (green) shown on each micrograph. The size of each nanoparticle is indicated.

Fig. 2 A-B: Real (ε_1) and imaginary (ε_2) parts of dielectric function of Hg nanoparticles integrated from their central regions (5 nm) plotted as function of energy loss. The insets are zoomed areas for highlighting their behavior as a function of energy loss.

Fig.3 A-B: Real (ε_1) and imaginary (ε_2) parts of dielectric function of Hg nanoparticles integrated from their surfaces (3 nm) plotted as function of energy loss.

References

[1] A. R. Krauss et.al, Phy. Rev. B, **13** (8), 3419-3423 (1976).
[2] T. Inagaki et al., Phy. Rev. B, **23** (10), 5246-5262 (1981).
[3] W. E. Mueller et al., Phy. Rev. Lett., **23** (18), 1037-1038 (1969).
[4] J. M. Howe et al., J. Micro. **53** (4), 339-351 (2004).
[5] A. T. J. Hayward, J. Phys. D, vol. 4, 951-955 (1971).
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