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Optical and electrophysical characteristics of liquid carbon

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The general approach to the determination of optical characteristics of liquid carbon by laser reflectometry proposed in this study has shown that liquid carbon is a dielectric material in the optical range at pressures of up to several Gbar.

Studies on the electrophysical and optical properties of liquid carbon have led to extremely contradictory results and have not answered the question of whether this material is a conductor[1–3] or dielectric.[4,5] Judging from direct measurements of the specific resistance, liquid carbon is a dielectric at pressures below 4 kbar, for example, along the liquid–vapour equilibrium curve up to 6000 K (ρ = 1000 μΩ cm),[4,5] and a conducting medium with ρ = 150 μΩ cm (at high pressures of 10–110 kbar)[1] or ρ = 30±8 μΩ cm (at 40 bar and 4450 K).[2] It has also been reported that the conducting phase exists at higher pressures, whereas the dielectric phase exists at lower pressures.[6]

Reflectometric measurements of optical constants (refraction *n* and attenuation *k* indices) of the liquid carbon arising upon melting of graphite under the action of laser radiation[7] make it possible to determine, using the Drude theory,[8] the specific resistivity of the liquid phase at optical frequencies $\rho(\omega)$ from equation (1),

$$\rho(\omega) = \frac{4\pi(1+\omega^2\tau^2)}{\omega_{\mathrm{pl}}^2\tau} = \frac{2\pi}{n(\omega)^2 k(\omega)\omega} \qquad (1)$$

where ω_{pl} is the plasma frequency of the medium, ω is the cyclic frequency of laser radiation and τ is the electronic relaxation time. This value is an estimate of the upper limit for the static specific resistance $\rho(0)$. However, the non-justified use of the optically 'thick' film approximation (reflection only by the melt phase) in the calculations of $n(\omega)$ and $k(\omega)$ in all the published examples has resulted in the ω_{pl}, τ and $\rho(0)$ values being at variance with the corresponding values for analogous materials (Se, Ge, Sn).[7] Apparently, the assumption that the film is optically 'thin' would be a more versatile approach in this case.

In this study, using the method of laser reflectometry, we discovered interference of laser radiation in the layered air–melt–graphite medium. The angular dependence (Figure 1) of the coefficient of reflection *R* for the second harmonic radiation (532 nm) of Nd:YAG laser with an intensity of 0.01–0.7 GW cm^{-2}, sufficient for graphite to melt in a nanosecond pulse (0.02 GW cm^{-2}), exhibits local maxima and minima typical of radiation interference in an optically 'thin' film (reflection on the film and on the support).

The interference effect on the reflection and transmission coefficients of thin-film optical coatings has been considered in detail in the theory of propagation of electromagnetic waves in layered media.[8] Allowing for the absorbing character of the melt and of the graphite support itself, the dependence of *R* on the film thickness *Y* can be expressed by equation (2),

$$R(Y) = \frac{\rho_{12}^2 + \rho_{23}^2\exp(-2\alpha Y) + 2\rho_{12}\rho_{23}\cos(\varphi_{23} - \varphi_{12} + {}^{2\pi}\!/_{\lambda}\, nY)\exp(-\alpha Y)}{1 + \rho_{12}^2\rho_{23}^2\exp(-2\alpha Y) + 2\rho_{12}\rho_{23}\cos(\varphi_{12} + \varphi_{23} + {}^{2\pi}\!/_{\lambda}\, nY)\exp(-\alpha Y)} \qquad (2)$$

where ρ_{12}^2, ρ_{23}^2, φ_{12} and φ_{23} are reflection and phase-shift coefficients at the air–melt (12) and melt–graphite (23) interfaces[8] and *n* and α are refraction index and absorption coefficient of liquid carbon, respectively. The parameters ρ_{12}^2, ρ_{23}^2, φ_{12}, φ_{23} and α which appear in the *R*(*Y*) equation are functions of the variables *n* and *k* (the refraction and attenuation indices of liquid carbon at a particular radiation frequency ω); therefore, in general, *R*(*Y*) varies as a function of *n*, *k* and *Y*.

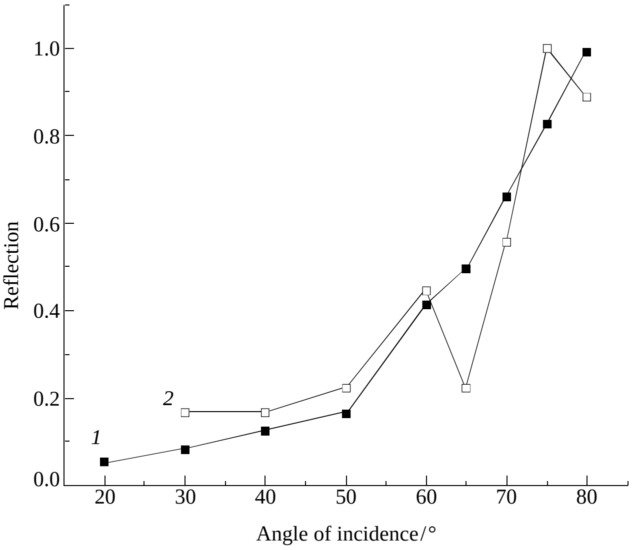

Figure 1 Angular dependence of the reflection coefficient of graphite at various intensities of the incident light: (*1*) 0.012 GW cm^{-2} (below the melting threshold equal to 0.02 GW cm^{-2}), (*2*) 0.58 GW cm^{-2} (above the melting threshold), relative standard deviation 12%.

To calculate the *n* and *k* values in the present study we used the reported values of the reflection coefficients of liquid carbon at various *Y* values. By varying *n* and *k*, we obtained the best agreement between the *R* values found from equation (2) for each of the known fixed *Y* and experimental *R* values, which changed with a certain step within the confidence interval of their determination. The correspondence was defined as the minimum sum of squared deviations of calculated *R* values from experimental *R* values for each fixed *R*(*Y*) combination at various *Y* values (the least-squares method).

The reflection coefficient of graphite remains virtually constant up to the threshold density of energy $\varepsilon_{\mathrm{thres}}$ = 140 mJ cm^{-2} in a broad spectral range of graphite *R*(300–700 nm) = 0.29–0.30.[7] This permits use of the above *R* value as the initial conditions *R*(*Y* = 0).

The results of reflectometric studies for liquid carbons resulting from melting of graphite by pico- and femtosecond laser pulses are markedly dissimilar. When the duration of a laser pulse is *ca.* 20 ps, transfer of the electron subsystem energy to the phonon subsystem and melting and vaporisation of the substance do occur over a period of 1 ps;[7] however, there is not enough time for the heat conduction mechanism to switch on. Acoustic relaxation (expansion of the heated substance accompanied by a decrease in its density and its internal pressure) in the region of radiation absorption occurs over a period of $\alpha^{-1}C_{\mathrm{snd}} \approx$ 8–10 ps for the absorption depth of α^{-1}(500–700 nm) = 30 nm[7] (this is the minimum size of the absorption area with respect to the characteristic sizes of the focusing area of 10–100 μm) and with the sound velocity in the direction perpendicular to the surface (base plane) $C_{\mathrm{snd}} = 3200$ m s^{-1}.[10] When the density of energy increases to 5–6 $\varepsilon_{\mathrm{thres}}$ (0.7–0.9 J cm^{-2}), $R(Y, 532$ nm$)$ reaches a steady-state value of 0.06 ± 0.01,[11] which apparently corresponds to a film thickness of 0.18 μm.[9]

This steady-state thickness of the melt film on the graphite surface was found by transmission electron microscopy for remelted highly oriented pyrolytic graphite at an energy density ε of the nanosecond-pulse radiation above 1.8 J cm^{-2}.[9] In this case, the loss of heat due to heat conductivity at this particular laser pulse duration results in $\varepsilon_{\mathrm{thres}} = 0.8$ J cm^{-2}; therefore, the effective ε value, with total ε being 1.8 J cm^{-2}, is only 1 J cm^{-2}, which approximately coincides with the ε value corresponding to the steady-state R ($Y = 0.18$ μm, $\lambda = 532$ nm) = 0.06 ± 0.01.

Conversely, in the case of femtosecond laser pulses (90 fs),[7] acoustic relaxation lags behind the transfer of energy from the electron subsystem to the phonon subsystem and behind melting and vaporisation processes; therefore, carbon, which apparently becomes molten under the action of radiation with an energy density of more than $\varepsilon_{\mathrm{thres}}$, occurs at a pressure of tens of Gbar over a period of several picoseconds after the pulse.[7] Note that the reflection coefficient of a film of this ‘compressed’ liquid carbon with a thickness of α^{-1}(500–700 nm) = 30 nm is somewhat larger than that of graphite. For this thickness, $R(Y = 30$ nm, $\lambda = 550$ nm$) = 0.30 \pm 0.01$, $R(Y = 30$ nm, $\lambda = 620$ nm$) = 0.31 \pm 0.01$, $R(Y = 30$ nm, $\lambda = 700$ nm$) = 0.30 \pm 0.01$.[7] However, according to reflectometric measurements with time resolution,[7] within 20 ps after the acoustic relaxation, the $R(Y = 30$ nm, $\lambda = 550$–700 nm$)$ value decreases to 0.26 ± 0.01 as a result of transformation of the ‘compressed’ liquid carbon into ‘normal’ carbon.

Using combinations of $R(Y = 0, \lambda = 300$–700 nm$) = 0.29 \pm 0.01$ with $R(Y = 0.18$ μm, $\lambda = 532$ nm$) = 0.06 \pm 0.01$ and $R(Y = 30$ nm, $\lambda = 550$–700 nm$) = 0.26 \pm 0.01$ for liquid carbon after acoustic relaxation (‘normal’ liquid carbon) and $R(Y = 30$ nm, $\lambda = 550$ nm$) = 0.30 \pm 0.01$, $R(Y = 30$ nm, $\lambda = 620$ nm$) = 0.31 \pm 0.01$ and $R(Y = 30$ nm, $\lambda = 700$ nm$) = 0.30 \pm 0.01$ for ‘compressed’ liquid carbon, we calculated their refraction and attenuation indices by the algorithm described above. In the case of ‘normal’ liquid carbon, the following values were obtained: $n(532$ nm$) = 0.84 \pm 0.01$, $k(532$ nm$) = 0.45 \pm 0.15$ and $n(550$–700 nm$) = 0.9 \pm 0.1$, $k(550$–700 nm$) = 0.5 \pm 0.1$. For ‘compressed’ liquid carbon, the optical parameters were $n(550$–700 nm$) = 2.6 \pm 0.1$, $k(550$–700 nm$) = 0.45 \pm 0.05$. Our results differ noticeably from published data [$n(620$ nm$) = 1.35$, $k(620$ nm$) = 1.5$ for ‘compressed’ liquid carbon,[7] $n(532$ nm$) \approx 1$, $k(532$ nm$) < 0.5$ for ‘normal’ liquid carbon] calculated using an optically ‘thick’ melt film approach.[11]

The resulting values of optical constants for ‘compressed’ (apparently, liquid) carbon and ‘normal’ liquid carbon, which has experienced acoustic relaxation, indicate that the carbon liquid phase is a dielectric material in the optical range for a broad range of pressures, if the real part of the dielectric constant $\mathrm{Re}\,\varepsilon(\omega) = n(\omega)^2[1 - k(\omega)^2]$ is used as the criterion of the ‘conductor–dielectric’ transition. The positive sign of $\mathrm{Re}\,\varepsilon(\omega)$ in the visible region means that the ‘conductor–dielectric’ transition of the molten phase occurs in the infrared region. In addition, note that the refraction index of ‘compressed’ liquid carbon (2.6 ± 0.1) is close to the corresponding parameter of diamond [$n(589$ nm$) = 2.4$],[12] which is formed in the same pressure range, *i.e.* at pressures of several Gbar.

The upper values of static specific resistance $\rho(0)$ of both phases of liquid carbon estimated according to equation (1), which are equal to 5000 μΩ cm (the ‘normal’ phase) and 500 μΩ cm (the ‘compressed’ phase), are in reasonable agreement with published data.[7] The observed decrease in the specific resistance of liquid carbon with a pressure increase is a matter of common knowledge.

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