# Experimental and *ab initio* investigations of microscopic properties of laser-shocked Ge-doped ablator

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Plastic materials (CH) doped with mid-Z elements are used as ablators in inertial confinement fusion (ICF) capsules and in their surrogates. Hugoniot equation of state (EOS) and electronic properties of CH doped with germanium (at 2.5% and 13% dopant fractions) are investigated experimentally up to 7 Mbar using velocity and reflectivity measurements of shock fronts on the GEKKO laser at Osaka University. Reflectivity and temperature measurements were updated using a quartz standard. Shocked quartz reflectivity was measured at 532 and 1064 nm. Theoretical investigation of shock pressure and reflectivity was then carried out by *ab initio* simulations using the quantum molecular dynamics (QMD) code ABINIT and compared with tabulated average atom EOS models. We find that shock states calculated by QMD are in better agreement with experimental data than EOS models because of a more accurate description of ionic structure. We finally discuss electronic properties by comparing reflectivity data to a semiconductor gap closure model and to QMD simulations.

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# I. INTRODUCTION

Inertial confinement fusion (ICF) experiments on large laser facilities use a spherical capsule made of an ablator material and filled with a deuterium-tritium (DT) mixture in cryogenic and gaseous form. These experiments aim at producing an implosion of the capsule in order to create a hot spot at its center, where density and temperature are expected to become high enough to trigger thermonuclear reactions. In the direct drive scheme, laser beams interact with the ablator material, creating a low density plasma corona which accelerates the DT fuel inward. In the indirect drive scheme, the capsule is enclosed in a high-Z material (such as Au or U) hohlraum and the laser beams are pointed towards the inner walls. Laser light is then converted into a wide band x-ray spectrum which ensures a spatially uniform implosion. Radiation produced by the hohlraum is mainly thermal, but the interaction of laser beams with hohlraum gas filling and walls also produces out of equilibrium *M*-band radiation from which the DT fuel must be shielded in order to avoid preheat phenomena.

Plastic (CH) materials doped with mid-Z elements such as germanium are interesting ablators for ICF capsules. Their low initial mass density ensures high ablation velocity and mitigates the development of Rayleigh-Taylor (RT) instabilities at the ablation front. Mid-Z atoms of the dopant play a crucial role in both direct and indirect drive schemes. In the direct drive scheme, previous works on brominated plastic [1] and germanium or silicon-doped plastic [2,3] have shown that the presence of mid-Z atoms in the plastic ablator reduces laser imprinting and creates a radiation ablation front ahead of the ablation front generated by electron conduction. These two mechanisms increase the ablation velocity as well as the density scale length of the blowoff plasma, which in turn improve the ablative stabilization of RT growth. In the indirect drive scheme, capsules use the so-called graded dopant design [4-9], in which doped layers of plastic buried deep into the ablator material are used to shield the fuel from *M*-band hard x rays.

During implosion of the capsule, ablator material thermodynamic path crosses the so-called warm dense matter (WDM) region of temperature (T)-density  $(\rho)$  phase diagram  $(T \sim 1-100 \text{ eV}, \rho \sim 0.01-10\rho_0)$  in which matter is found in the form of a weakly ionized, strongly coupled, partially degenerate plasma. Hydrodynamic simulation tools use tabulated equations of state (EOSs) such as QEOS [10] or SESAME [11]. These provide thermodynamics and transport properties of materials over several decades in density and temperature by combining various models. Each of these models were validated in limited regions of the phase diagram, but none of them provide an accurate description of WDM, which is described by means of interpolations and empirical correction terms.

Several laser experiments have been performed previously on CH materials and provided measurements of the principal Hugoniot curve as well as shock front reflectivity. Most of these experiments studied commercial polystyrene [12–15], as well as CH foams [16-18]. Br-doped CH was also studied [19], and more recently glow-discharge polymers used in ICF capsules [20]. In parallel, progress in large-scale computing allowed state-of-the-art theoretical description of the WDM regime and beyond using *ab initio* quantum molecular dynamics (QMD). In particular, calculation of reflectivity has been done for a variety of materials (e.g., Refs. [21-24]) because it allows comparison with experiments and validates description of electronic properties. Recent QMD studies on CH ablators produced EOS and transport coefficient data along isochores [25,26], principal Hugoniot [27,28], as well as over extended  $(\rho, T)$  regions of the phase diagram [29–31]. These studies however focused on idealized undoped CH materials.

To improve our knowledge of complex ICF capsule relevant materials, we recently initiated a series of experiments on

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TABLE I. Initial densities in  $g/cm^3$ , real parts of optical indexes at 532 and 1064 nm wavelengths, and atomic fractions of samples.

	$ ho_0$	<i>n</i> <sub>532</sub>	<i>n</i> <sub>1064</sub>	С	Н	0	Ge
CHOGe[2.5%]	1.286	1.58	1.56	0.328	0.56	0.087	0.025
CHOGe[13%]	1.762	1.615	1.59	0.221	0.56	0.089	0.13

the GEKKO laser facility at Osaka University [32] in which we performed Hugoniot EOS and reflectivity measurements of Ge-doped CH with dopant fractions 2.5% and 13% in atomic proportions. These materials are used in ICF capsule designs for the laser Mégajoule in France and in their surrogates for reduced-scale experiments. Analysis of these materials showed that their structure and composition is more complex than commercially available polymeric CH such as polystyrene. Spherical capsules used for ICF experiments cannot be fabricated using common CH polymers. Instead, CH is deposited on a foam mandrel (dissolved thereafter by pyrolysis) using glow discharge polymerization (GDP). This process produces an amorphous structure (the term polymerization is indeed misleading). Moreover, upon storage, oxygen from ambient air humidity is introduced in the bulk and can reach atomic fractions of about 5% for undoped GDP-CH [33]. When doping with Ge, we found that the oxygen atomic fraction rises to up to 9%. Bulk properties of the samples are indicated in Table I. More details about the characterization of the samples can be found in Ref. [32]. Ge-doped CH samples under study will then be designated CHOGe[2.5%] and CHOGe[13%].

CHOGe is initially a transparent insulator. As it is compressed along the Hugoniot, it becomes increasingly reflective since more electrons populate the conduction band. In a previous work [32], this behavior was tracked using reflectivity and temperature measurements and described using a semiconductor gap closure fitting model [34] (designated as gap closure model thereafter). Such modeling however makes some simplified assumptions, since it considers a perfect gas of free electrons and therefore does not consider intrinsic properties of shocked CHOGe such as detailed ionic and electronic structures.

In this work, we attempt to improve the description of shocked CHOGe structure and electronic properties by simulating pressure and reflectivity of experimentally measured ( $\rho$ , T) Hugoniot states using QMD code ABINIT [35–37]. To this extent, we used previously published [32] shock speed and Hugoniot density and updated and completed the temperature and reflectivity of a quartz reference. Quartz reference data were obtained by measuring quartz temperature and 532- and 1064-nm reflectivity as a function of shock speed. 532-nm reflectivity and temperature data are in good agreement with previous studies [38,39], and new 1064-nm reflectivity data are presented.

Data were then compared to models and dedicated QMD calculations. The first step of QMD calculations was to compare simulated and experimental shock pressure P using measured temperature T and density  $\rho$ . For both Ge dopant fractions, QMD simulations show that ionic structure has to be taken into account in order to describe shock compressibility

of data, whereas average atom EOS models predict stiffer behaviors.

In the second step of QMD calculations, we compute optical properties either by using Kubo-Greenwood formalism or by applying Drude-Sommerfeld modeling of density of states (DOS) calculations. QMD results are compared with data and with a semiconductor gap closure fitting model. While no approach is fully satisfactory to describe our data sets in their entirety, we discuss the relevance of each modeling. Finally we compare our data to previously published data on polystyrene and find that Ge doping, even at fractions as high as 13%, does not have a strong influence on electronic properties of the shock front.

# II. SHOCK REFLECTIVITY AND TEMPERATURE MEASUREMENTS

Pressure, density, temperature, and reflectivity were measured along the principal Hugoniot of CHOGe using the GEKKO laser facility at the Osaka University. The GEKKO laser facility is comprised of three double-frequency laser beams at 527 nm and nine triple-frequency laser beams at 351 nm. Laser energy was varied from 500 J at 527 nm to 800 J at 351 nm and contained into a 2.5-ns-square pulse focused onto a 1-mm or 600- $\mu$ m focal spot using Kinoform phase plates. In these experiments, a shock was transmitted from a quartz plate to a CHOGe sample. Since both materials are transparent, it is possible to probe speed, reflectivity, and emissivity of the shock front in both materials as a function of time, allowing measurements of shock pressure P, reflectivity R, and temperature T. Quartz EOS and reflectivity have been the subject of numerous studies [40,41], allowing quartz to be used as a reference material.

In this section, we present measurements of quartz temperature and reflectivity, including data at 1064 nm that were not available in the literature to our knowledge. We then use the calibrated optical properties of shocked quartz to extract CHOGe reflectivities and temperatures that were used for and compared to QMD calculations.

# A. Experimental configuration

Targets for the study of CHOGe were multilayered and consisted of a polypropylene ablator material, a metallic pusher (Al or Au), a polished quartz reference material, and the sample of CHOGe, for which atomic fractions of Ge were either 2.5% or 13% (Fig. 1). An additional 0.1- $\mu$ m layer of aluminum was deposited on the CH ablator front surface to avoid laser shine-through at the beginning of the irradiation.

Diagnostics provided measurements of shock velocity, reflectivity, and visible self-emission, from which were deduced pressure, density, and gray-body equivalent temperature along the Hugoniot curve. Since quartz and CHOGe samples were transparent, we were able to optically monitor shock propagation in quartz followed by transmission in CHOGe.

Shock velocity and reflectivity were measured using the line-imaging Velocity Interferometers System for Any Reflector (VISAR) [42]. The probe beam reflecting on the shock front was provided by a Q-switched YAG laser emitting at 532 and 1064 nm and with a pulse duration of  $\approx 10$  ns.



FIG. 1. (Color online) VISAR measurement of shock speed and reflectivity in quartz and CHOGe.

Upon reflection on the shock front, the VISAR probe beam is Doppler shifted, which causes a fringe shift on the exit beam splitter of the VISAR. Fringes are imaged onto a streak camera system allowing time resolved measurement of shock velocities. Reflectivities can in principle be deduced from fringe intensities. However, in most cases these must be corrected from absorption phenomena (e.g., caused by hard x rays or energetic particles produced in the laser-plasma corona) occurring in transparent materials. Such corrections are not always feasible within reasonable uncertainties.

Brightness temperature was measured by a streaked optical pyrometer (SOP) diagnostic consisting of a visible streak camera coupled to an image relay and narrow band (38 nm around 455 nm) filter. Given all the characteristics of the optical system and energy response of the streak camera and associated charge-coupled device (CCD), the number of counts can be linked to the apparent gray body temperature using a simple relationship of the form

$$T = T_0 / \ln[1 + (1 - R)A/I],$$
(1)

where the natural logarithm arises from the inversion of the Planck function, (1 - R) is the gray body emissivity,  $T_0$  and A are constants determined by the experimental setup, and I is the number of counts recorded on the CCD. The constant  $T_0$  is given by  $T_0 = \frac{hc}{k_B\lambda_0}$ , where  $\lambda_0$  is the center wavelength of the narrow-band filter. This technique allows absolute measurement of gray body temperature, but, like reflectivity, also often requires corrections due to absorption in the materials.

A now common way to bypass these shortcomings is to measure optical properties of the shocked transparent material relative to a quartz reference. During the last decade, quartz has been the subject of several experimental studies in which its Hugoniot EOS was measured with high precision using laser [40], Z-pinch facilities [41], and underground nuclear explosions [43]. A single fit of all data from these experiments was given in Ref. [29]. Reflectivity at 532 nm and temperature of quartz were also absolutely calibrated as function of quartz shock velocity [38,39]. Using these calibrations, one can deduce the reflectivity and shock temperature of quartz directly from shock velocity measurement. Therefore, when a shock is transmitted from a quartz layer to another transparent sample material, the reflectivity (R) and temperature (T) of the shocked sample can be deduced relative to quartz R and T, independently of the measuring system absolute calibration. In the case absorption of the transparent materials is not known, this method is valid only around the quartz-sample interface (that is within a time window of typically a few 100 ps), supposing that the optical path of the probe beam (or self-emission signal) does not vary appreciably, allowing quartz and sample R and T to be measured in the same conditions. This method applies for shock pressures in the Mbar range, under which quartz is transparent or absorbing. For very high pressures (above  $\sim 20-30$  Mbar), this method may become invalid because of radiation losses in the quartz shock front.

#### B. Shocked quartz reference reflectivity and temperature

We performed a series of laser shots dedicated to the measurement of quartz temperature and reflectivity at both 532- and 1064-nm wavelength in order to provide calibration curves for optical measurements of CHOGe shock states. Targets were similar to the ones used for the CHOGe shots and consisted of a 15- $\mu$ m polystyrene ablator, a 40- $\mu$ m aluminum pusher. and 50- $\mu$ m quartz with antireflection coating for both VISAR wavelengths in order to eliminate ghost fringes. The aluminum pusher was glued onto the quartz window and glue thickness was estimated to be  $\approx 1 \ \mu m$ . The initial reflectivity of these targets at the Al/quartz interface was estimated by measuring the ratio of fringe intensities to fiducial intensity on a reference shot and comparing to the ratio given by a calibrated Al mirror. We found that the initial Al/Qz interface reflectivity is  $0.85 \pm 0.15$ , which is in agreement with the ideal value of 0.877, but with a high uncertainty due to the probe beam shot-to-shot variations in the spatial pattern of intensity and temporal shape. Therefore, the glue layer at the Al/quartz interface might induce a systematic uncertainty, but its contribution is most likely small compared to other random errors associated with probe beam variations.

Each shot generated a decaying shock in quartz for which shock speed, reflectivity, and gray-body temperature were measured (Fig. 2). For these shots, no signs of preheating at the Al/quartz interface (such as loss of reflectivity, fringe shift or self-emission prior to shock breakout) were detected. Shock speed was measured on the 532-nm VISAR for which the sensitivity was 2.88 km s<sup>-1</sup> fringe<sup>-1</sup> and the uncertainty was  $\sim 1/20$  fringe, corresponding to 0.15 km s<sup>-1</sup>. Reflectivity of the shock front in quartz at 532 and 1064 nm was measured by taking fringe intensity profiles, corrected by subtraction of background noise and temporal shape of the probe beam and normalized to the initial Al/quartz interface reflectivity. Quartz gray body equivalent temperature was measured as a function of decaying shock velocity using SOP absolute calibration data and correcting by the reflectivity measured at 532 nm.

A total of nine shots were analyzed in this way and produced a set of reflectivity data as a function of shock speed, depicted in Fig. 3. Comparing our data at 532 nm to data obtained on the Omega laser facility [38], we find slightly higher values in our explored shock speed range of 10–17 km/s. This data set is however in better agreement with another data set published in the Supplemental Materials of Ref. [39]. As expected for a Drude-like simple metal with no band structure, infrared



FIG. 2. (Color online) Data set obtained in a single shot on a quartz target used to produce quartz reflectivity and temperature calibration data. (a) Shock velocity measured in quartz (color scale is quartz shock pressure deduced from the fit given by Ref. [29]), (b) shock reflectivities measured at 532 nm in green and at 1064 nm in red, (c) number of counts measured on SOP (color scale indicates equivalent gray body temperature using 532-nm reflectivity and absolute calibration of the diagnostic). Insets in (b) and (c) display VISAR and SOP images respectively.

reflectivity at 1064 nm has higher values: here shocked quartz is  $\approx$ 50% more reflective at 1064 nm than at 532 nm.

Quartz reflectivity data *R* can be fitted as a function of shock speed  $U_s$  by Hill equation  $R = R_0 + (R_{max} - R_0)[U_s^n/(U_s^n + D^n)]$ , where  $(R_{max} = 0.32, R_0 = 0.00765, n = 9.9765, D = 15.103 \text{ km/s})$  for 532-nm data and  $(R_{max} = 0.4, R_0 = 0.050053, n = 11.329, D = 14.207 \text{ km/s})$  for 1064-nm data. In the case of 532-nm data,  $R_{max}$  was forced to the Omega experiment saturation value.  $R_{max}$  for the 1064-nm wavelength was estimated by extrapolating recent QMD calculations published by Qi *et al.* [44] and was set to 0.4.



FIG. 3. (Color online) Quartz reflectivity as function of shock speed calibration. Color code is green for 532-nm wavelength, red for 1064 nm, and gray for Omega measurements at 532 nm [38].



FIG. 4. (Color online) Quartz temperature as function of shock speed calibration. Color code is orange for our data, gray for Omega data [38], light red for SESAME EOS no. 7385, light orange for SESAME EOS no. 7383, and light green for Kerley EOS.

We find that temperature data *T* as a function of shock speed  $U_s$  (Fig. 4) is in good agreement with previous measurements performed on the Omega facility and can be fitted using a power law  $T = \theta_0 + AU_s^{n_T}$ , where ( $\theta_0 = -0.073$  eV, A = 0.00196,  $n_T = 2.411$ ). We note however that quartz shock temperature data is below SESAME tables no. 7383 and no. 7385. Our data set crosses the Hugoniot curve given by the Kerley equation of state, but no phase transitions are discernible within the data.

#### C. CHOGe reflectivity and temperature data extraction

We updated CHOGe reflectivity and temperature data previously published in Ref. [32]. These were reanalyzed relative to quartz reflectivity and temperature as determined in the previous section. CHOGe reflectivity data were extracted by subtracting background noise from the images, then correcting fringe intensities from the probe beam temporal pulse shape (either using fiducial intensity or reference shot intensity), and finally normalizing to the quartz reflectivity before transmission from the quartz layer to the CHOGe sample. Fits of the data from Fig. 3 were used to obtain quartz reflectivity before transmission in CHOGe. CHOGe reflectivity was averaged after shock transmission from quartz and uncertainties were taken from the standard deviation of CHOGe corrected intensity around its mean value.

Grey-body equivalent CHOGe temperature was measured using SOP signal intensities before and after shock transmission from quartz to CHOGe. Since calibration equation (1) is valid regardless of the target material, we can isolate the calibration constant  $A = I(e^{T_0/T} - 1)/(1 - R)$ , where R, T, and I can be replaced by either quartz parameters before shock transmission ( $R_{Qz}$ ,  $I_{Qz}$ ,  $T_{Qz}$ ) or CHOGe reflectivity after transmission ( $R_{CHOGe}$ ,  $I_{CHOGe}$ ). This leads to a simple expression of CHOGe shock temperature relative to quartz temperature:

$$T_{\text{CHOGe}} = \frac{I_0}{\ln \left[\frac{I_{Qz}(1 - R_{\text{CHOGe}})}{I_{\text{CHOGe}}(1 - R_{Qz})}(e^{T_0/T_{Qz}} - 1) + 1\right]}$$



FIG. 5. (Color online) Sample data set used for the extraction of reflectivity and temperature in CHOGe using quartz reference. (a) Shock velocity profile (the discontinuity at 2.2 ns is due to the change of refractive index which modifies the VISAR sensitivity), (b) reflectivities at 532 nm (green) and 1064 nm (red) normalized to quartz calibrated reflectivity, (c) SOP intensity signal (in counts). The vertical dashed gray line shows the quartz/CHOGe interface and insets show experimental images. In (b) and (c), the regions shaded in gray are where the averages are calculated.

An example of raw data is given in Fig. 5. The time resolution of the VISAR and SOP diagnostics are dominated by the point spread function of the streak cameras, which translates into an effective time resolution of  $\approx 150-200$  ps. Reflectivities and SOP counts were averaged 100-300 ps before and after shock transmission, depending on the image quality. These averages were separated by  $\approx 200$  ps in order to not be compromised by the instrument time resolution.



FIG. 6. (Color online) CHOGe reflectivity as function of shock speed: (a) 2.5% dopant fraction, (b) 13% dopant fraction. Color code is blue for 2.5% dopant fraction and red for 13% dopant fraction. For both dopant fractions, symbols circled in green and dark red are measurements at 532 and 1064 nm, respectively. Shaded regions are guides to the eye.



FIG. 7. (Color online) CHOGe temperature as function of shock speed: (a) 2.5% dopant fraction, (b) 13% dopant fraction. Color code is blue for 2.5% dopant fraction and red for 13% dopant fraction. Lines show EOS models QEOS-Yukawa (dotted), QEOS (dashed), and QSEM (continuous).

Extracted data for all shots (Fig. 6) show that for both dopant fractions reflectivity increases as a function of shock speed, since the temperature increases and the gap closes along the Hugoniot. Infrared (1064 nm) reflectivity was measured on some of the shots and is found to be systematically above visible (532 nm) data, which is characteristic of a metal-like state for which high reflectivities are observed in the infrared range.

Temperature data for both dopant fractions are plotted in Fig. 7. Uncertainty is  $\pm 16\%$  and arises from scatter and various sources of error in the absolute calibration of the SOP system. Data are also compared to EOS models described thereafter. Temperature data for 2.5% dopant fraction favor QEOS (quotidian equation of state) models over QSEMs (quantum semiempirical model), while the trend is reversed for highly doped CH (13% dopant fraction) for which a full quantum description of the electrons by QSEMs seems more relevant.

### D. Equation of state models

Hugoniot data are compared to several tabulated average atom EOS models, all of which are based on the hypothesis that the Helmholtz free energy can be written as the sum of three contributions arising from ions, electrons, and a cold curve, and each of these contributions is calculated separately.

The quotidian equation of state (QEOS) model [10] is entirely analytic and can be scaled using only atomic number Z and atomic mass A, allowing calculation of EOS for *a priori* any material: an average atom is used in the case of CHOGe. The ionic part uses a Debye solid model and a Lindemann melting law. The electronic part is given by Thomas-Fermi (TF) theory which also allows A and Z scaling of all thermodynamic variables. TF modeling of the electrons produces high pressures (~Mbar) at normal density and temperature. To retrieve bulk properties at normal conditions, a chemical bond correction is applied [45]. Experimental results are also compared with a modified form of QEOS called QEOS Yukawa in which the ionic component of the fluid phase is described using a Yukawa potential [46]. This modification of the QEOS model allows a better transition to the ideal gas limit at high temperatures. Finally, a quantum semiempirical model (QSEM) uses the one component plasma (OCP) model for the description of the ions, and a full quantum treatment of the electrons using the Inferno [47] option implemented in the VAAQP code (variational average atom in quantum plasmas) [48].

Such models are widely used in tabulated forms in hydrodynamic simulation tools because these allow a coherent description of thermodynamic states over several decades of densities and temperatures. However, we will show in the next section that these lack precision in the description of the microscopic properties of materials in the WDM region.

# **III. SHOCK STATES QMD SIMULATIONS**

# A. Inputs to calculations and method

Simulations are performed using the *ab initio* plane wave density functional theory (DFT) code ABINIT [35-37]. DFT is applied together with generalized gradient approximation [49]. Simulations are performed in the framework of the projector augmented wave (PAW) method [50,51]. The PAW datasets are generated using four outer electrons  $(2s^22p^2)$  and a cutoff radius  $r_c = 1.10a_B$  for carbon, using six outer electrons  $(2s^2 2p^4)$ and a cutoff radius  $r_c = 1.20a_B$  for oxygen. The cutoff radius for hydrogen is  $r_c = 0.80a_B$ . For germanium, we use the PAW dataset including semicore states  $(3s^23d^{10}3p^2)$  with a cutoff radius  $r_c = 1.5a_B$  which has been benchmarked extensively against physical properties obtained from experiments [52,53]. We use a plane wave basis with an energy cutoff of 40 Ha. The cubic simulation box includes 200 atoms for all cases, 44 C, 112 H, 18 O, and 26 Ge for CHOGe[13%] and 65 C, 112 H, 17 O, and 6 Ge for CHOGe[2.5%].

To simulate CHOGe mixture at a given thermodynamic state, molecular dynamics (MD) simulations are performed at  $\Gamma$  point for representation of the Brillouin zone. At each ionic time step, forces are computed within DFT using the Hellman-Feynman theorem. We assume thermodynamic equilibrium with ionic temperature equal to the electronic temperature. The electron temperature is controlled by the width of the Fermi-Dirac distribution. The ion temperature is controlled in the isokinetics ensemble where the velocities are rescaled at every time step to maintain the desired temperature. Before reaching a stable ion structure, the system relaxes for a few hundreds of time steps. After equilibration, pressure fluctuates around a well-defined value and thermodynamic parameters can be obtained.

When performing molecular dynamics simulation for a system with different masses among the species, the maximum time step is limited by the lightest element in the simulation cell. This is a bottleneck in the case of CHOGe mixture since we have to deal with a very light element H (1 g/mol) and a heavy element Ge (73 g/mol) in the same simulation box. For hydrogen at the highest temperature considered here, the appropriate time step should be 0.1 fs. This time step is so short that we would need thousands of steps to sample correctly the configurational ensemble for germanium and then to deduce averaged properties. This is a real difficulty, since the PAW data sets for germanium impose a high cutoff energy and the temperatures considered here impose to compute



FIG. 8. (Color online) Radial distribution function (rdf) for CHOGe[13%] at 4.15 g/cm<sup>3</sup> and 0.47 eV: (a) H-H rdf, (b) C-H rdf, (c) C-C rdf. Color code is green for calculations with real masses and dotted pink for calculations with all masses set to carbon mass.

explicitly a high number of bands. This high cutoff and high number of bands increase the computational time compared to simulations for pure CH as performed in Refs. [28] and [29]. In QMD, the ion dynamics is classical and the equilibrium distribution of a system of particles is not dependent on the masses of individual particles. The masses only affect the dynamics, not the ensemble. This idea has been exploited in numerous studies to achieve a better sampling (see for example Refs. [54,55] and references therein). Therefore we are free to choose appropriate masses without affecting thermodynamic properties. The simplest way is to increase the masses of the hydrogen atoms to attenuate the velocity of the hydrogen; as a consequence the time step can be increased. Following this change in the masses, we cannot obtain any time dependent properties from the QMD simulation like diffusion coefficient or viscosity. Figure 8 shows an example of the radial distribution function obtained for simulations performed with the hydrogen mass set to the carbon one  $(12 \text{ g/cm}^3)$  compared to a reference simulation with the real hydrogen mass. For each case the time step is set accordingly. Once the equilibrium is reached, the radial distribution functions are equivalent and we obtain the same pressures. All simulations are then performed with all masses set to the carbon mass (12 g/mol) and with 1 fs for the time step. We also checked that optical properties calculations (described in the next section) were not affected by this technique.

# **B.** Shock pressure calculations

Shock states for CHOGe[2.5%] and CHOGe[13%] were simulated using experimentally measured density  $\rho$  and temperature *T*. Since 16% uncertainty on temperature is quite large, we also simulated extrema of error bars for each density. Note that these calculations are not QMD Hugoniot calculations *per se*. Doing so would mean solving the Hugoniot equation by interpolating around previously

TABLE II. Densities, compressions, and temperatures input in QMD simulations and resulting pressures.

	$\rho$ (g/cm <sup>3</sup> )	$ ho/ ho_0$	<i>T</i> (eV)	P (Mbar)
CHOGe[2.5%]	2.9	2.25	$0.6 \pm 0.096$	$0.85 \pm 0.07$
	3.34	2.59	$1.12 \pm 0.179$	$1.71\pm0.16$
	3.5	2.71	$2.3\pm0.368$	$2.95\pm0.31$
	3.86	2.99	$4.3\pm0.688$	$5.63\pm0.7$
CHOGe[13%]	4.15	2.36	$0.47\pm0.075$	$0.6\pm0.03$
	4.54	2.58	$0.54 \pm 0.086$	$0.92\pm0.03$
	4.86	2.77	$1.66\pm0.266$	$2.14\pm0.3$
	5.28	2.99	$3 \pm 0.48$	$3.5 \pm 0.4$
	5.58	3.17	$5.15\pm0.824$	5.7±0.9

calculated isotherms [27,28,56,57] as well as computing the initial internal energy  $E_0$  of the unperturbed CHOGe samples, requiring precise information about the initial structure which is not available. Here we choose to start from the experimental data as start points to QMD calculations.

Each ( $\rho$ , *T*) configuration was simulated over simulations times rangin 1–3.5 ps in order to reach pressure stabilization and to generate a sufficient number of ionic configurations for the subsequent optical properties calculations (see Sec. IV). Pressure root mean square around average value is typically <0.05–0.1 Mbar depending on the ( $\rho$ , *T*) configuration. The main contribution on simulated pressure error bar comes from the uncertainty on the experimentally measured temperature and reaches up to 0.9 Mbar for the highest shock states. Results are given in Table II.

Experimental data, EOS models, and QMD simulation results are plotted as function of compression  $\eta = \rho/\rho_0$  in Fig. 9. We also show Hugoniot measurements of Barrios [15] (reanalyzed using quartz standard from Ref. [29]) and QMD simulations [28] of polystyrene. All experimental data sets from polystyrene CH and CHOGe show a similar dependence of pressure as a function of compression, indicating that the presence of a Ge dopant and initial amorphous structure of GDP does not have a measurable influence on Hugoniot compressibility in the explored pressure range. In particular, compressibility  $\kappa = \eta^2 \partial \eta/\partial p$  of all CH data sets decreases at compression  $\rho/\rho_0 \approx 2.6 \times$ .

Hugoniot curves from all average atom EOS models (QEOS, QEOS-Yukawa, and QSEM) barely differ one from another and show very little sensitivity to the dopant fraction when plotting as a function of compression. Agreement with data is found above compression  $2.6 \times$ , under which predicted shock pressure is overestimated. In contrast to EOS models, QMD simulations are in much better agreement with data over the explored compression range. In particular, we note that QMD calculations accurately reproduce the higher compressibilities of CHOGe below compression  $2.6 \times$ . For large Ge dopant fractions of 13%, QMD simulations slightly overestimate compressibility and simulated shock pressures are below experimental data. For these compressions, simulated temperatures need to be increased by  $\approx 0.5 \text{ eV}$ in order to retrieve experimental pressures. Nevertheless, considering experimental error bars in density, QMD is in overall better agreement with experimental data than EOS models. Results by Hu et al. agree better with 13% Ge data for



FIG. 9. (Color online) Pressure-compression Hugoniots for CHOGe[2.5%] and CHOGe[13%]. Experimental data (filled circles) are compared to tabular EOS models (lines) and QMD calculations (triangles). Color code is blue for 2.5% dopant fraction and red for 13% dopant fraction. Our results are compared with previously published works on polystyrene by Barrios [15] (experimental data, gray filled circles) and Hu [28] (QMD simulations, gray filled triangles). Data from Barrios [15] were reanalyzed using quartz standard from Hamel [29].

which temperatures and compressions are similar. Measured CHOGe[2.5%] temperatures as a function of compression are higher, leading to higher QMD pressures.

# C. Ionic radial distribution functions

Examination of ionic radial distribution functions g(r) gives interesting insight into materials properties and shows how QMD simulations retrieve compressibility of data sets.

CHOGe[2.5%] simulated at its lowest shock state measured in the experiment can be considered as a molecular liquid in which C-C, C-O, C-H, and O-H bonds are still present [Fig. 10(a)]. As soon as temperature increases to  $\approx 1$  eV, only C-C bonds are seen. For higher shock temperatures, all types of bonds disappear and a simple liquid state is obtained [Fig. 10(b)].

CHOGe[13%] simulations display similar features for the lowest shock state [Fig. 11(a)]. C-C bonding however stays strong up to compression  $\approx 2.6 \times$ , corresponding to  $\rho \approx 4.7 \text{ g/cm}^3$  [Fig. 11(b)].

For both dopant fractions, these C-C bonds remain up to compression  $2.6 \times$  allowing vibrational modes to absorb the heat which leads to a larger compressibility compared to a completely dissociated system. This effect is even stronger in CHOGe[13%] for which experimental temperature does not vary appreciably below compression  $2.6 \times$ .

Our QMD calculations therefore show that shocked CHOGe[2.5%] and CHOGe[13%] can be described as molecular liquids up to  $\approx 2.6 \times$  compression. Since EOS models use an average atom to describe mixtures and do not describe



FIG. 10. (Color online) Radial distribution functions (rdf) for CHOGe[2.5%]: (a) rdf at the lowest simulated shock state ( $\rho = 2.9 \text{ g/cm}^3$ , T = 0.6 eV), (b) evolution of C-C rdf along the simulated shock states.

molecular liquids, this explains why experimental shock pressures below  $2.6 \times$  compression are lower than EOS model predictions. For higher compressions, our QMD calculations show that the CHOGe systems dissociate while agreement is found between experimental data and EOS models. From this we can conclude that the average atom EOS models can describe shocked CHOGe mixtures as long as these systems are hot enough to be dissociated.

#### D. Conclusion on shock states QMD calculations

To conclude on shock states calculations, we showed that QMD gives a better description of our data sets compared to EOS models. For both dopant fractions, QMD provides a coherent scenario to explain discrepancies between data and average atom EOS models for the lowest densities obtained in



FIG. 11. (Color online) Radial distribution functions (rdf) for CHOGe[13%]: (a) rdf at the lowest simulated shock state ( $\rho = 4.15 \text{ g/cm}^3$ , T = 0.47 eV), (b) evolution of C-C rdf along the simulated shock states.



FIG. 12. (Color online) Reflectivity of shock front in CHOGe[2.5%] and CHOGe[13%] at 532 nm: experimental data (filled circles); Drude modeling of the electrons (using QEOS ionization: dashed lines; using gap closure fitting model: continuous lines; and using QMD density of states: filled triangles), and Kubo-Greenwood QMD calculations (open triangles).

our experiments. Higher compressibility of the measured and calculated shock states shows that detailed ionic structure will have to be taken into account in EOS modeling. In the meantime, when using these models in hydrodynamic simulation codes for practical applications such as ICF capsule design or interpretation of integrated experiments, it is important to keep in mind that observables such as shock speeds may be overestimated due to inaccuracies in compressibility of CH ablator materials at ~Mbar pressures.

# **IV. OPTICAL PROPERTIES CALCULATIONS**

Shock front reflectivity data previously presented in Fig. 6 are shown as a function of shock density in Figs. 12 and 13 and compared to various modelings described thereafter.

The reflectivity at 2.5% dopant fraction shows a smooth increase for both 532- and 1064-nm wavelength while at 13% dopant fraction, a saturation at 0.4 of the reflectivity at 532 nm occurs when complete dissociation of the sample is reached at  $\approx$ 4.75 g/cm<sup>3</sup>. This reflectivity plateau suggests a metallic state as already seen in hydrogen [58].

Reflectivity measured during the experiments is the reflectivity of the shock front in its propagation medium, that is at the interface between shocked and unshocked material, as recalled by Hu *et al.* [28]. Reflectivity  $R(\omega)$  is given by

$$R(\omega) = \frac{[n(\omega) - n_0(\omega)]^2 + [k(\omega)]^2}{[n(\omega) + n_0(\omega)]^2 + [k(\omega)]^2},$$
(2)

where  $n(\omega)$  and  $k(\omega)$  are respectively the real and imaginary part of the index of refraction and where 0 denotes the initial state of the CHOGe material in which the shock propagates [the initial absorption in CHOGe  $k_0(\omega)$  was measured to be  $\sim 10^{-4}$  and is neglected here]. The complex index of refraction



FIG. 13. (Color online) Reflectivity of shock front in CHOGe[2.5%] and CHOGe[13%] at 1064 nm: experimental data (filled circles), Drude modeling of the electrons (using QEOS ionization: dashed lines; using gap closure fitting model: continuous lines; and using QMD density of states: filled triangles), and Kubo-Greenwood QMD calculations (open triangles).

is calculated from the complex dielectric function  $\epsilon(\omega)$ , which describes the response of a medium to an external electric field, and which is defined by

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = [n(\omega) + ik(\omega)]^2$$

where  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  are respectively the real and imaginary parts of the dielectric function and are given by the complex electrical conductivity  $\sigma(\omega)$ , whose real and imaginary parts are  $\sigma_1(\omega)$  and  $\sigma_2(\omega)$ :

$$\epsilon_1(\omega) = 1 - \frac{4\pi}{\omega}\sigma_2(\omega)$$
$$\epsilon_2(\omega) = \frac{4\pi}{\omega}\sigma_1(\omega).$$

Modeling reflectivity thus reduces to expressing either the complex dielectric function  $\epsilon(\omega)$  or the electrical conductivity  $\sigma(\omega)$ . We now compare experimental data to results given by applications of the Drude model and by Kubo-Greenwood formalism.

# A. Drude modeling of reflectivity

In the Drude model [59], reflectivity is calculated by considering a free electron gas. The response of a free electron oscillating under the influence of an external electric field is described in terms of an equation of motion which contains a damping term  $\tau^{-1}$  corresponding to the mean electron collision frequency. Working out solutions of the motion equation with Maxwell relations, one can find an expression for the complex electrical conductivity  $\sigma(\omega)$ :

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau},$$

where  $\sigma_0 = n_e e^2 \tau / m_e$  is the dc electrical conductivity. The real and imaginary parts of the complex dielectric function are

$$\epsilon_1 = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2},$$
  
$$\epsilon_2 = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}.$$

Essential inputs to this model are the electron collision time  $\tau$  and density  $n_e$  contained within plasma frequency  $\omega_p = (n_e e^2 / \epsilon_0 m_e)^{1/2}$ . The simplest way to express the electron collision time is to consider only electron-ion collisions.  $\tau$  can then be taken at the Ioffe-Regel limit [60]  $\tau_{IR} = d_i / \langle v_e \rangle$ , with  $\langle v_e \rangle$  being the mean electron velocity and  $d_i = 2(3/4\pi n_i)^{1/3}$ being the average distance between ions deduced from ionic density  $n_i$ . In its original form, the Drude model is fully classical: the velocity is that of a perfect gas  $[v = (3k_BT/m_e)^{1/2}]$  and the electron density was given by the number of atoms times the number of valence electrons. Improvements of this model include the so-called Drude-Sommerfeld model, for which the electron velocity depends only on the electron density through the Fermi velocity  $v_F = \frac{\hbar}{m_e} (3\pi^2 n_e)^{1/3}$ . Electron density  $n_e$  is still needed and in the case of a shock front for which ionization is a priori unknown, the electron density has to be adjusted in the model in order to match experimental data. We now describe two ways to parametrize the Drude model: (1) using a gap closure model, and (2) using densities of states (DOS) calculated by QMD simulations.

### 1. Thomas-Fermi pressure ionization within QEOS model

The most straightforward way to use the Drude-Sommerferld is to input electron density calculated using  $n_e = Z_{\text{TF}}^* n_i$  where  $n_i$  is the ion density and  $Z_{\text{TF}}^*$  is Thomas-Fermi pressure ionization that is used in QEOS and given by the analytical formula of More [61] which expresses  $Z_{\text{TF}}^*$  as a function of A, Z,  $\rho$ , and T, thereby allowing straightforward calculation of reflectivity along the Hugoniot for any material. However, as recalled in Sec. II D, the electron pressure is overestimated by Thomas-Fermi theory in the WDM region, which translates into reflectivities that strongly overestimate experimental data.

#### 2. Gap closure model

In the semiconductor band gap closure fitting model [34], the rise of reflectivity of an insulator along its principal Hugoniot is calculated using a semiconductor description of the electrons. The energy of the semiconductor band gap  $E_g$  is a linearly decreasing function of density on the Hugoniot  $E_g = a - b\rho$ . Electron density and velocity in the conduction band are given by semiconductor theory, assuming nondegenerate bands and effective masses set to 1:

$$n_{e} = 2 \left( \frac{m_{e} k_{B} T}{2\pi \hbar^{2}} \right)^{3/2} F_{1/2}(-E_{g}/2k_{B}T),$$
  
$$\langle v_{e} \rangle = \left( \frac{2k_{B} T}{m_{e}} \frac{F_{3/2}(-E_{g}/2k_{B}T)}{F_{1/2}(-E_{g}/2k_{B}T)} \right)^{1/2},$$

where  $F_{1/2}$  and  $F_{3/2}$  are Fermi integrals whose general form is  $F_m(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^m dx}{1 + \exp(x - \eta)}$ . These quantities depend

upon temperature only, which is deduced from fitting of experimental data [62]. The ion-electron collision rate is given by  $\tau = \gamma \tau_{IR}$  where  $\tau_{IR}$  is the Ioffe-Regel limit and  $\gamma$  is a factor close to unity. The fitting parameters of this model are gap closure dependence coefficients (*a* and *b*) and the  $\gamma$  factor. This model allows negative values of the gap because of the exponential function in the Fermi integrals used in the calculation of  $n_e$  and  $\langle v_e \rangle$ , allowing a continuous semiconductor to metal transition along the Hugoniot.

Fits were constrained in order to obtain gap energies at normal density close to 4–7 eV which is the typical band gap value measured for CH [63]. Fitting coefficients (*a*, *b*,  $\gamma$ ) obtained in this way were (8.5 eV, 1.77 eV cm<sup>3</sup> g<sup>-1</sup>, 1.59) for CHOGe[2.5%] and (8.77 eV, 1.13 eV cm<sup>3</sup> g<sup>-1</sup>, 1.58) for CHOGe[13%]. Only data measured at 532 nm were used for fitting. Because of the scarcity of infrared data, fitting curves at 1064 nm are calculated using coefficients (*a*, *b*,  $\gamma$ ) obtained with 532-nm data.

A semiconductor gap closure fitting appears to be in good agreement with data at 532-nm wavelength and predicts semiconductor states with an average gap energy  $\approx 2 \text{ eV}$  for CHOGe[2.5%] data and  $\approx 4 \text{ eV}$  for CHOGe[13%] data. The rise of reflectivity along the Hugoniot is well described, but not the saturation of reflectivity. Saturation of reflectivity is not described by this model because of the simplified free electron gas picture which produces a continuous rise of conduction electron density (and a slow decay of the electron collision time) along the Hugoniot. Saturation of 532-nm reflectivity is observed at  $\approx 3.85$  g/cm<sup>3</sup> for CHOGe[2.5%] and at  $\approx 5$  g/cm<sup>3</sup> for CHOGe[13%]. It was also observed for undoped CH [15] as discussed in the conclusion of this section. Good agreement is also found at 1064-nm wavelength except for the highest densities for which saturation of reflectivity is also ignored by the model.

#### 3. QMD simulations densities of states and occupancies

Another way to calculate the electron density required in the Drude model is to use the electron density of states (DOS) provided by QMD calculations and count the number of electrons with energies exceeding the Fermi level. Electron DOS were calculated by averaging over several ionic configurations with a 2 × 2 × 2 Monkhorst-Pack *k*-point grid sampling of the first Brillouin zone in the cubic cell. Occupancies are given by taking the product of the total DOS and of the Fermi-Dirac distribution function  $f(E) = \{\exp[(E - E_F)/k_BT] + 1\}^{-1}$  (where  $E_F$  is the Fermi energy) and were normalized to the total number of electrons used in simulations (848 for CHOGe[2.5%] and 1352 for CHOGe[13%]). When  $k_BT \ge$  $2E_g$ , the Fermi-Dirac distribution function spreads over the conduction band: conducting electronic states are occupied and free electrons contribute to the measured reflectivity.

Both dopant fractions display common features (Figs. 14 and 15). The peak seen at  $\approx 25$  eV below the Fermi energy is due to Ge bound 3*d* electrons, which means that most Ge electrons stay localized around the nuclei. Only electrons in the outer 4*p* shell (3.89 eV below Fermi energy) are delocalized and contribute to electrical conduction. At the Fermi energy, a pseudogap (that is with a minimum energy above zero) can be



FIG. 14. (Color online) Density of states (continuous lines) and occupancies (dashed lines) in CHOGe[2.5%] at (a)  $\rho = 2.9$  g/cm<sup>3</sup>, T = 0.6 eV, (b)  $\rho = 3.8$  g/cm<sup>3</sup>, T = 4.3 eV. Color code is blue for QMD calculations and gray for gap closure model.

seen for the lowest densities and temperatures but is completely closed for the highest shock temperatures.

Mean ionization can be obtained by integrating occupancies above Fermi energy and then dividing by the total number of ions. Drude reflectivities obtained in this way give a somewhat better agreement with CHOGe[2.5%] experimental data compared to Kubo-Greenwood calculations, except at the lowest densities for which the calculated reflectivities are still overestimated. Similar trends are found for CHOGe[13%]: calculated reflectivity increases with shock densities, but saturation of reflectivity at highest densities is not reproduced.

It is straightforward to compare QMD DOS to the gap closure model, which considers a three-dimensional Fermi gas of electrons, distributed over a valence band and a conduction band separated by an energy gap  $E_g$ . The gap closure model DOS in the valence band is calculated using Sommerfeld theory and is proportional to the root square of energy  $E^{1/2}$ . The valence band energy is calculated by



FIG. 15. (Color online) Density of states (continuous lines) and occupancies (dashed lines) in CHOGe[13%] at (a)  $\rho = 3.5$  g/cm<sup>3</sup>, T = 0.35 eV, (b)  $\rho = 5.58$  g/cm<sup>3</sup>, T = 5.15 eV. Color code is red for QMD calculations and gray for gap closure model.

taking the Fermi energy at zero temperature at which CHOGe is an insulator. Similarly, the DOS in the conduction band is proportional to  $(E - E_g)^{1/2}$ . Note that the DOS in the conduction band calculated by QMD simulations also follows a  $E^{1/2}$  dependency for energies above the pseudogap.

The main difference between the gap closure model and QMD simulations is the number of conducting electrons. For both dopant fractions, total occupancies above the Fermi energy range  $10^{-4}$ – $10^{1}$  when calculated with the semiconductor model and from  $10^{1}$  to  $10^{2}$  in QMD simulations. These large differences explain the low density differences in the reflectivities calculated using these modelings.

### B. Kubo-Greenwood formalism

To obtain the optical properties, we select equally spaced ionic configurations along the equilibrated part of the trajectory. These are used to start precise static DFT calculations in order to apply the Kubo-Greenwood formula [64–66]. The real part of the optical conductivity  $\sigma_r(\omega)$ , in atomic units, is given by

$$\sigma_{1}(\omega) = \frac{2\pi}{3\omega V} \sum_{\mathbf{k}} W(\mathbf{k}) \sum_{j=1}^{N_{\rm B}} \sum_{i=1}^{N_{\rm B}} \sum_{\alpha=1}^{3} [F(\epsilon_{i,\mathbf{k}}) - F(\epsilon_{j,\mathbf{k}})] \\ \times |\langle \Psi_{j,\mathbf{k}} | \nabla_{\alpha} | \Psi_{i,\mathbf{k}} \rangle|^{2} \delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \omega).$$
(3)

Here  $W(\mathbf{k})$  is the *k*-point weight in the Brillouin zone using the Monkhorst-Pack scheme. The summations over *i* and *j* run over  $N_{\rm B}$  discrete Kohn-Sham eigenstates considered in the electronic structure calculation. The three spatial directions are averaged by the  $\alpha$  sum and *V* is the volume of the simulation box.  $F(\epsilon_{i,\mathbf{k}})$  is the Fermi distribution function and describes the occupation of the *i*th band corresponding to the energy  $\epsilon_{i,\mathbf{k}}$  and the wave function  $\Psi_{i,\mathbf{k}}$  at **k**. The  $\delta$  function has to be broadened because a discrete energy spectrum results from the finite simulation volume [67].

The imaginary part  $\sigma_2$  of the conductivity can be derived from the  $\sigma_1$  using the Kramers-Kronig relation, with the principal value of the integral over  $\sigma_1$ :

$$\sigma_2(\omega) = -\frac{2}{\pi} P \int \frac{\sigma_1(\nu)\omega}{(\nu^2 - \omega^2)} d\nu \tag{4}$$

The dielectric function  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ , the real part  $n(\omega)$ , and the imaginary part  $k(\omega)$  of the refraction index derive from the knowledge of the complex electrical conductivity. In particular, the reflectivity at normal incidence is obtained using Eq. (2).

The results from different snapshots from the same simulation run are averaged in order to reduce statistical uncertainties. All molecular dynamics calculations are performed at the  $\Gamma$  point for representation of the Brillouin zone. The  $\Gamma$ point sampling is expected to be a good approximation for calculating the structure and dynamics, but is not enough for accurate calculation of electronic structure such as that needed for the calculation of optical properties. To compute optical properties, we then run a DFT calculation with a  $2 \times 2 \times 2$  Monkhorst-Pack grid [68]. We consider electronic states occupied down to  $10^{-6}$  which means around 1600 bands are explicitly computed for the highest temperature considered here. Convergence of the calculations was checked by varying the width of the  $\delta$  function in Eq. (3), *k*-point sampling and the number of bands. Differences were seen at energies beyond 10 eV, which is far beyond photon energies used by the VISAR diagnostic. The integral in the Kramers-Kronig transform was calculated to an energy of 2 Ha ( $\approx$ 54 eV).

Applying Kubo-Greenwood formalism to ionic configurations calculated by QMD gives good agreement with data for the highest densities obtained in the experiment (see open triangles in Figs. 12 and 13). The vanishing of bonds, as discussed in the previous section, produces an upward shift in the reflectivities since more electrons become available for conduction. Another interesting aspect of Kubo-Greenwood calculations is the ability to reproduce saturation of reflectivity at high densities, as measured for CHOGe[13%] as well as in the work on polystyrene of Hu et al. [28]. We also find good agreement with infrared 1064-nm reflectivities measured at the highest experimental densities for both dopant fractions. This indicates that the high density measurements at 1064 nm are likely to have reached the saturation value of reflectivity. However, for the lowest densities achieved in our experiments, reflectivities are overestimated.

#### C. Conclusion on reflectivity QMD calculations

To conclude on reflectivity analysis, it is interesting to plot as a function of compression our data and previously published experimental and simulation works [15,28] (Fig. 16). When



FIG. 16. (Color online) 532-nm wavelength shock reflectivity as function of compression. Experimental data were obtained on CHOGe at GEKKO (blue and red filled circles for 2.5% and 13% dopant fractions), and on polystyrene at Omega [15] (green filled circles). Data from Barrios [15] were reanalyzed using quartz standard from Hamel [29]. Calculated reflectivity data for CHOGe were obtained using QMD and Kubo-Greenwood formalism (open triangles) or Sommerfeld modeling (filled triangles). Open triangles linked by a dashed line used inputs from the QEOS-Yukawa EOS in order to simulate the nonmetal to metal transition. QMD simulations of polystyrene by Hu [28] (green triangles) were obtained using Kubo-Greenwood formalism.

comparing experimental data, we find that CHOGe reflectivity as a function of compression along the Hugoniot does not differ noticeably from polystyrene, even when the dopant fraction is high. This is also coherent with examination of electron DOS discussed earlier which showed that most electrons from Ge are localized near their nuclei and contribute very little to conduction. Putting this result in perspective with ICF means that when using CH with a dopant fraction of Ge as an ablator material in the capsule, electronic properties play a role for the x-ray absorption properties of the outer layers of the capsule but will have no effect on at least the first shock, since the pressure range explored in our experiments extends up to  $\approx$ 7 Mbar and the first shock generated by the NIF or LMJ laser pulse is at  $\approx$ 2.5 Mbar.

When plotting as a function of compression, our QMD Kubo-Greenwood calculations show that no strong dependence of Ge dopant fraction is found. In both polystyrene and CHOGe, the saturation of shock reflectivity is reproduced by this simulation method. However, reflectivity at lower density is overestimated. Sommerfeld modeling of QMD calculated densities of state is in better agreement with intermediate experimental densities but also fails at reproducing lowest density data. Underestimation of gap by QMD simulations leading to reflectivities higher than measured data has already been discussed in other works and is also seen in Hu et al. [28] simulations for the lowest compression used in their work. The sharp rise of reflectivity due to the transition from nonmetal to metal is not predicted in the experimental compression range. In order to locate such a transition as predicted by QMD simulations, we extended our calculations to lower shock states. Since these were not measured, we used  $(\rho, T)$  inputs from the QEOS-Yukawa model which agrees best with the lowest temperature data points (see Fig. 7). Inputs to lower shock states than the ones we measured were (2.5 g/cm<sup>3</sup>, 0.2 eV) for CHOGe[2.5%], and (3.5 g/cm<sup>3</sup>, 0.35 eV) and  $(3 \text{ g/cm}^3, 0.14 \text{ eV})$  for CHOGe[13%]. We then find simulated nonmetal to metal transitions at compression  $\approx 2 \times$  for CHOGe[2.5%] and  $\approx 1.7 \times$  for CHOGe[13%]. Our QMD simulations therefore reproduce this transition but not at the correct density. This inaccuracy can be attributed to the lack of knowledge on the exact exchange-correlation potential used with DFT formalism which considers noninteracting electrons in an effective potential. As shown by this analysis, Kubo-Greenwood formalism used in this work also contributes to overestimation of reflectivity.

#### V. CONCLUSION

In this work, we updated and completed temperature and reflectivity data of laser-shocked CHOGe[2.5%] and CHOGe[13%] materials used for experimental ICF capsule studies. We used the quantum molecular dynamics ABINIT code to perform simulations of the measured shock states. Shock density and temperature measurements as well as chemical compositions of these materials were used as input to our calculations. The first step of this study was to compare shock pressures calculated by QMD to the ones predicted by tabulated EOS models and measured in the experiment. We found that for the lowest densities (i.e., up to at least  $\approx 2.6 \times$  compression), C-C bonds were still present and contribute to the compressibility of the materials. Such features are not included as of today in EOS models which do not describe molecular liquids and predict stiffer behaviors. These findings motivate for the use of QMD simulations to map the WDM region of tabulated EOS models.

In the second part of this study, we compared reflectivity data at 532 and 1064 nm with different models. The gradual rise of reflectivity along the Hugoniot can be fitted using a gap closure model, but at the cost of fitting parameters. Moreover, this model cannot reproduce the saturation of reflectivity for the highest densities. In these regimes, the temperature is still too low to completely ionize all atoms so carrier density is still expected to increase in the frame of the Drude model. Retrieving saturation of reflectivity can only be achieved using massive QMD calculations, outlining the complexity of the description of such states of matter for which electronic and ionic structures need to be accurately described. Dealing with complex mixtures such as CHOGe, which includes insulators and semimetal germanium, also complicates state-of-the-art QMD Kubo-Greenwood calculations which underestimate the gap energy of weakly ionized states. The developments presented here can most likely be extended to different varieties of CH ablators, since dopant fraction of a mid-Zelement such as Ge (Z = 32) only changes bulk parameters such as initial density, but has little influence on electronic properties.

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