Reflectivity measurements on hot reactive liquids using a FIR laser

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The experimental procedures and precautions required to measure liquid-alloy reflectivities with a cw far infrared (FIR) laser are described. The output of a carefully stabilized optically pumped FIR laser was channeled to a melted sample contained in a silica holder under a He atmosphere. By maintaining specular reflection and alloy homogeneity, reflectivities reproducible to ±7% were routinely obtained.

I. Introduction

Far infrared (FIR) lasers are well suited to measuring temperature-dependent optical constants. They provide relatively intense monochromatic radiation at any of several hundred frequencies. The conventional FIR tool, Fourier transform spectroscopy, which is more appropriate for broadband constant-temperature measurements, is hampered by low power levels. Previous FIR laser work[1] on liquids has been confined to conditions near STP. This paper describes the application of a FIR laser to measurements of the reflectivity of volatile and reactive liquid metal alloys at elevated temperatures. The composition dependence of the reflectivity of Ga–Te liquid alloys is presented.

II. Experimental Arrangement

Figure 1 is a block diagram of the complete experiment. The laser system is quite similar to that of Bean and Perkowitz.[2] The CO_2 laser is a 25-W Coherent Radiation model 42 with an integral diffraction grating whose output mirror is vibrated at frequency ν_2 by a piezoelectric transducer (PZT). The grating is used to select the correct line from the CO_2 manifold, and the PZT modulation is used for cavity length stabilization.

The CO_2 laser output optically pumps methanol vapor (or other gases) flowing through a gold surface cylindrical waveguide (1-m × 2.5-cm diam), which comprises the FIR laser cavity. The input window is vibrated at frequency ν_3, and the laser output is sent on two alternate paths by a mechanical chopper at frequency ν_1.

One path leads via brass light pipes through a Fabry-Perot interferometer (used to check output wavelength) to a pyroelectric detector (REF. DET.). Its output is demodulated at frequencies ν_2 and ν_3 to adjust the laser cavities for maximum output either manually or under servo-loop control and at ν_1 to provide a reference signal for the reflectivity measurements.

The second path leads via brass light pipes to the sample furnace (described below) and then to another pyroelectric detector (SAMP. DET.) whose output is demodulated at frequency ν_1.[3] This signal and the reference signal are fed to a ratiometer (Ithaco model 3512) whose output is recorded on chart recorders; the ratiometer corrects for fluctuations in FIR laser output.

The optical furnace is an evacuable stainless steel cylinder containing a resistance-heated sample holder, thermocouples, and stirring rod. The walls and the lid, which contains light pipe and vacuum connections, are water-cooled. Details of the sample area are shown in Fig. 2. Silica was used to construct crucibles and stirrer to avoid contamination of the typically reactive liquid alloys. After passing through a 1.5-mm thick polyethylene window, the FIR radiation is channeled by replaceable stainless steel light pipes at 16° incidence to the sample surface. To ensure specular reflection from the sample surface, the height of which could vary with thermal expansion, evaporation, or meniscus changes, the height of the crucible assembly can be adjusted by an external micrometer. A window was not used to flatten the liquid surface and protect it from evaporation or reaction, because its absorption would restrict measurements to low frequencies, and the faces of the window could introduce spurious reflections or interference effects. The close proximity of light pipes to the relatively large-area liquid surface prevents the curved edges of the sample from reflecting radiation to the sample detector. Meniscus effects are limited to

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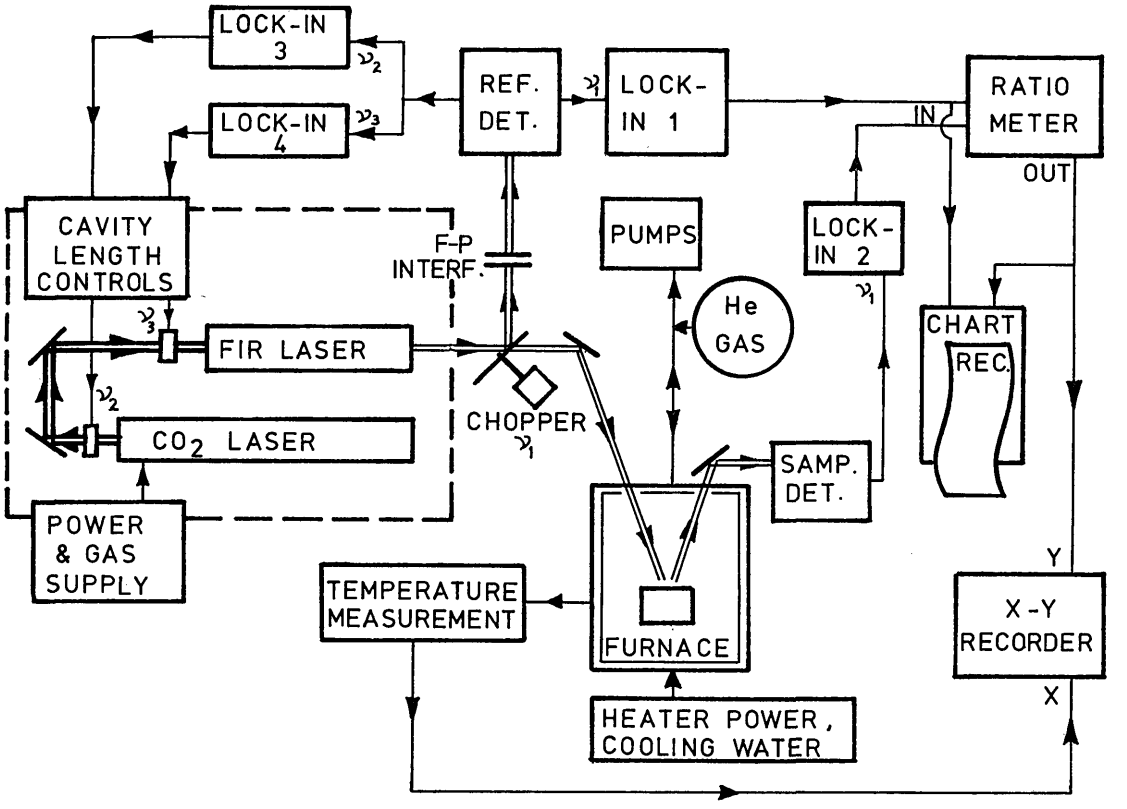

Fig. 1. Block diagram of the experiment.

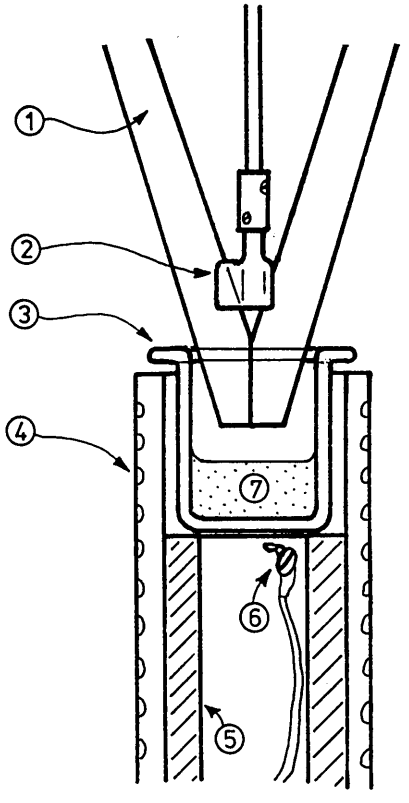

Fig. 2. Furnace sample-area detail: (1) stainless steel light pipe; (2) silica stirring rod; (3) silica crucible; (4) boron-nitride cylinder, supporting resistive heater wire; (5) adjustable-height sample support; (6) thermocouple; (7) sample ingot.

within 2 mm of the walls of the 25-mm diam crucible, and the beam diameter that could be collected by the exit light pipe was <15 mm.

Three methanol-vapor frequencies, 8.22, 17.5, and 84.1 cm^{-1}, spanning the FIR, were used in the experiments. The experimental procedure consisted first of measuring the compensated signal when a gold-coated glass disk was placed in the sample crucible at room temperature[4] and subsequently replacing it with an alloy sample, evacuating the furnace, and introducing a dry He atmosphere to reduce liquid evaporation. The sample was then heated through its melting point, and its height was optimized for maximum signal. To ensure alloy homogeneity, the stirring rod was lowered into the melt and rotated. Stirring, height optimization, and the reference measurement were repeated at least once per run. The true reflectivity was taken to be the ratio of the mean sample and reference measurements.

III. Results and Discussion

Initial test results using a solder metal sample, shown in Fig. 3, illustrate the problems that were encountered. In this case, the optimum sample height had been determined after initial melting. The apparently different melting and freezing temperatures are in fact due to hysteresis, resulting from too-rapid cooling. By restricting temperature changes to $\lesssim 12°$ C/min, liquidus temperatures in accord with published figures[5] were obtained. The differing reflectivities of samples 1 and

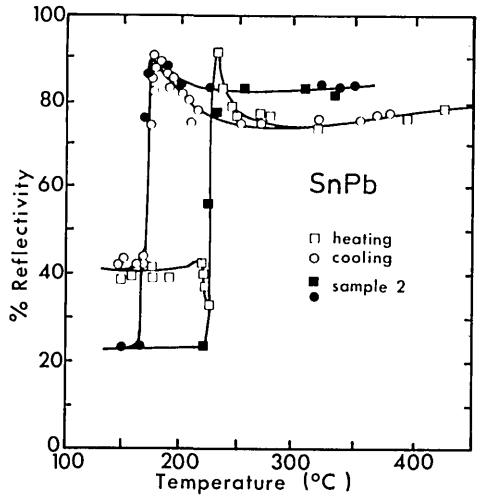

Fig. 3. Solder-metal reflectivity at 84.2 cm^{-1}. Discontinuities represent sample freezing/melting.

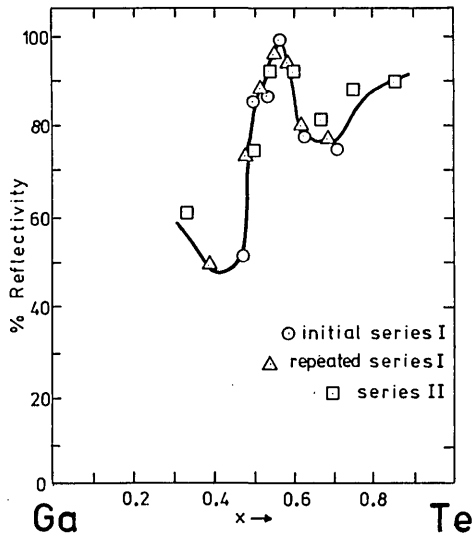

Fig. 4. Liquid $Ga_{1-x}Te_x$ alloy reflectivity at 84.2 cm^{-1} and T = 1200 K (927°C). Series I and II represent two sets of alloy samples.

2 are attributed to slight oxidation of the surface of solder sample 1. Subsequent repair of a furnace leak permitted evacuation to $<10^{-4}$ Torr and backfilling to a 2-atm pressure of dry He; this improved reproducibility. The solid-sample reflectivities still agreed less well, however, because of nonideal surface shapes (warping by thermal expansion upon freezing) and, for the alloys described below, formation of crystallites, which scattered radiation. For this reason, solid-sample reflectivities were not recorded in these experiments.

A final problem was interference effects at 8.22 cm^{-1} and occasionally at 17.5 cm^{-1}: by varying sample height, signal modulations of up to 20% were produced with maxima at $\lambda/2$ multiples in the micrometer position. This is ascribed to backreflection of radiation from the sample surface to the furnace entrance window and subsequent interference with an incoming ray. Backreflection was only possible for nonparaxial rays; long wavelength radiation was highly diverged by diffraction at the 2-mm diam hole of the laser exist mirror. Fixes, not yet carried out, could include replacement of the exit-hole configuration by a partially reflecting end mirror (at the expense of coupling-out higher-order modes) or enlargement of the exit hole (to the detriment of FIR output power).

Typical results after correction of the other problems are shown in Fig. 4. Liquid Ga–Te alloys at 927°C (1200 K) were individually and repeatedly measured. Reproducibility is ~±7%; about half of this random error is caused by shifts of the apparatus (and hence changes in light pipe channeling) upon interchange of the sample and reference crucibles in the furnace. Comparison to broadband reflectivity spectra for two liquid alloys, obtained by conventional Fourier transform spectroscopy, indicates that no systematic error is present. The Ga–Te data will be described in greater detail elsewhere.[6]

References

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3. Both detectors are Molectron model P4-43.
4. Initial tests indicated that nonlinearity or offsetting of the detector signal was not introduced by the blackbody radiation of the furnace.
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