

# Laser-Plasma Sourced, Temperature Dependent, VUV Spectrophotometer Using Dispersive Analysis

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## Abstract

We have developed a vacuum ultraviolet spectrophotometer with wide energy and temperature range coverage, utilizing a laser-plasma light source (LPLS). CO<sub>2</sub>-laser sample heating and time-resolved dispersive analysis. Reflection and transmission spectra can be taken from 1.7 to 40 eV (31–700 nm) on samples at 15–1800 K with a time resolution of 20–400 ns. These capabilities permit the study of the temperature dependence of the electronic structure, encompassing the effects of thermal lattice expansion and electron-phonon interaction, and changes in the electronic structure associated with equilibrium and metastable phase transitions and stress relaxation.

The LPLS utilizes a samarium laser-plasma created by a Q-switched Nd:YAG laser (500 mJ/pulse) to produce high brightness, stable, continuum radiation. The spectrophotometer is of a single beam design using calibrated iridium reference mirrors. White light is imaged off the sample in to the entrance slit of a 1-m polychromator. The resolution is 0.1 to 0.3 nm. The dispersed light is incident on a focal plane phosphor, fiber-optic-coupled to an image-intensified reticon detector. For spectroscopy between 300 and 1800 K, the samples are heated *in situ* with a 150 Watt CO<sub>2</sub> laser. The signal to noise ratio in the VUV, for samples at 1800 K, is excellent. From 300 K to 15 K samples are cooled using a He cryostat.

## 1. Introduction

The electronic structure embodies the most fundamental information available for a solid state material. Optical spectroscopy has been one of the first methods applied to materials in an attempt to determine their electronic structure. For the more extensively studied materials, such as alkali halides and covalent semiconductors, more advanced techniques are now applied such as the modulation spectroscopies, two photon spectroscopies and normal and inverse photo-emission to further elucidate the details of their electronic structure. The electronic structure of ceramic and optical materials based on oxides, nitrides, carbides, phosphates and borates have been less extensively studied to date, partially due to their large band gap energies, their highly insulating nature and the difficulties inherent in sample preparation of non-cleavable materials. Yet with the increasing importance and many new applications of ceramics and optical materials, there is a great demand for detailed electronic structure information [1].

Vacuum ultraviolet reflection and transmission measurements are powerful methods for the study of the electronic structure, producing detailed critical point and joint density of states information. They permit detailed exciton and absorption edge analysis and when coupled with Kramers-Kronig (KK) analysis [2], allow the determination of both the dielectric constant and optical properties. To derive high quality electronic structure information requires knowledge of the absolute magnitude of  $R$  and a sufficient energy range coverage so as to exhaust all of the valence interband tran-

sition. Exhausting the interband transitions allows the low and high energy extrapolations used in KK analysis to be realistic representations of the response of the material and minimizes the uncertainties introduced by the analysis.

With the advent of high-power pulsed lasers, laser plasmas have seen increasing applications as laboratory-based extreme ultraviolet (XUV) and vacuum ultraviolet (VUV) light sources for both line and continuum, time-resolved, radiation [3]. Applications of laser plasmas to date have included pumping of noble gas VUV lasers [4], X-ray lithography [5], and gas phase spectroscopy [6]. These applications have not required imaging of the plasma light or long term pulse stability. Our application of laser plasmas to spectroscopy of solids [7] demands long term stability of the laser position and intensity and the imaging and collection of the plasma light off of a solid sample and into a polychromator.

The advent of gated, multi-channel photon-counting detectors, makes possible dispersive, time-resolved VUV spectroscopy. Dispersive spectroscopy has the advantage of fast, real time acquisition of complete spectral regions. In addition time resolution permits detailed studies of kinetic phenomena involving features at different energies. It also becomes possible to study both excitation and relaxation phenomena by acquisition of both absorption and fluorescence spectra in the same instrument.

VUV spectroscopy over a wide temperature range serves three purposes. At low temperatures, the electronic structure can be determined with high resolution and minimal phonon broadening. As a function of temperature the effects of lattice expansion and the different regimes of weak and strong electron-phonon coupling can be probed. In addition detailed knowledge of the high temperature (> 1300 K) electronic structure of ceramic materials is essential to the high temperature processing and applications of these materials. An example of this is  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, an important polycrystalline ceramic whose processing and structural and optical applications involve temperatures of 1700 to 2100 K. The temperature dependence of the band gap ( $-1.1$  meV/K) leads to a  $10^5$  increase in the intrinsic electronic conductivity product  $\sigma_c \sigma_h$  with an associated change from ionic to predominantly electronic conductivity [8]. High temperature capabilities also permit the *in situ* study of electronic changes associated with high temperature processing such as phase transformations and crystallization.

## 2. The LPLS spectrophotometer

We have developed a new VUV spectrophotometer which combines wide energy and temperature range coverage with time-resolved dispersive analysis. This is accomplished

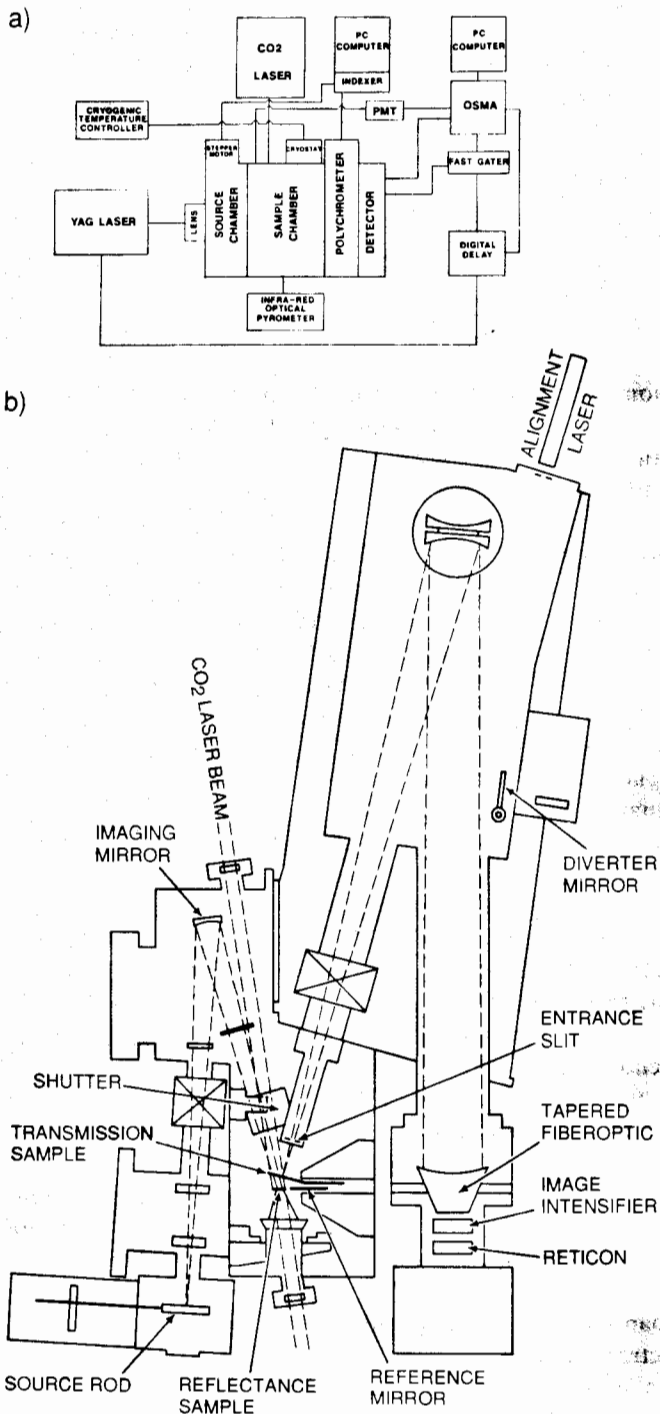


Fig. 1. (a) Block diagram of the major elements of the LPLS spectrophotometer, (b) schematic representations of the LPLS spectrophotometer.

through the use of the Laser Plasma Light Source (LPLS), CO<sub>2</sub> laser heating and cryogenic cooling and gated multi-channel detection. This spectrophotometer covers the energy range from 1.7 to 40 eV, on samples from 15 K to 1800 K with a time resolution of 20–400 ns.

The spectrophotometer, shown in Fig. 1, is normal incidence (all reflections at < 15°), single beam instrument with incident and sample intensities recorded sequentially. A calibrated iridium reference mirror is used in the sample position to record the incident intensity. Other possible designs for this system are a dual beam instrument based on matched detectors and beam splitters, or a single beam instrument with no reference mirror but requiring physical movement of the source or detector for incident and sample intensities.

Each of these alternative designs have their own limitations. For this instrument, uncertainties in the absolute magnitude of the reflectivity arise from the intensity and positional stability of the LPLS, the calibrated reference mirror reflectivities and the accuracy of the LPLS imaging off of the sample. We find the LPLS to be very stable and reproducible against the period of data acquisition. The reference mirrors are periodically checked against the reference calibration, and care is taken in sample positioning to maximize the collected light intensity.

### 2.1. LPLS

The LPLS is pumped by a 1.06 μm Q-switched Nd:YAG laser operated at 20 Hz, 500 mJ/pulse with an 8 nanosecond pulse width. As shown in Fig. 2, the laser beam is brought horizontally to the laser plasma chamber and is focused by a 300 mm lens external to the source chamber. The target is a solid rod, 2.5 cm diameter by 8 cm long, and it is helically stepped using a 100 thread per inch screw so as to provide a new metal surface for each shot. The rod is stepped approximately 200 μm on the surface between shots, with the laser focus at the rod on the order of 100 μm. The ablation of the rod produces a uniform removal of rod material. Periodic source chamber cleaning includes the resurfacing of the samarium rod on a lathe. To accommodate changes in the rod diameter, the source chamber can be raised to bring the rod surface back to the focal point of the optical system.

Contamination of the instrument and optics is a critical concern for the successful use of laser plasmas in solid sample spectroscopy. To overcome the contamination problems, the geometry is chosen so the plume of evaporated metal is at 45° between the horizontal incident laser beam and the vertical optical plane of the spectrophotometer. He and Ar filter gases are used for order sorting the plasma light, and to reduce the expansion rate of the plasma leading to higher source brightness. The filter gas inlet is positioned to deflect the plume away from both the incident laser window and spectrophotometer inlet. Differential pumping is required to attain the necessary instrument vacuum and minimize contamination of the plasma imaging mirror. Differential pumping is in two stages using a capillary plate with 50 μm pores and a hypodermic needle array, which are aligned on the optical axis and match the *f* number of the optical system. The source chamber is operated at 1 torr of He or Ar (except for measurements below the 50 nm cutoff of He), and mechanically pumped to aid the deflection of the plume by the filter gas jet. The differential pumping chamber is turbopumped and maintained at 10<sup>-4</sup> torr, while the hypodermic array yields system operating pressures of 1 × 10<sup>-7</sup> torr in the reflectometer chamber. This two stage differential pumping scheme leads to no measurable samarium deposition on the imaging mirror as measured by a quartz crystal oscillator placed above the hypodermic array. Rapid contamination of the capillary plate by samarium oxide can occur due to high levels of oxygen or water in the source chamber or filter gases, causing the source output to drop in minutes. With low oxygen partial pressures, metallic samarium deposition is seen, with minimal impact on source brightness.

2.1.1. Source brightness and stability. Laser plasmas have been created from many different metals and show different spectral characteristics [9]. Samarium, due to its *f* shell

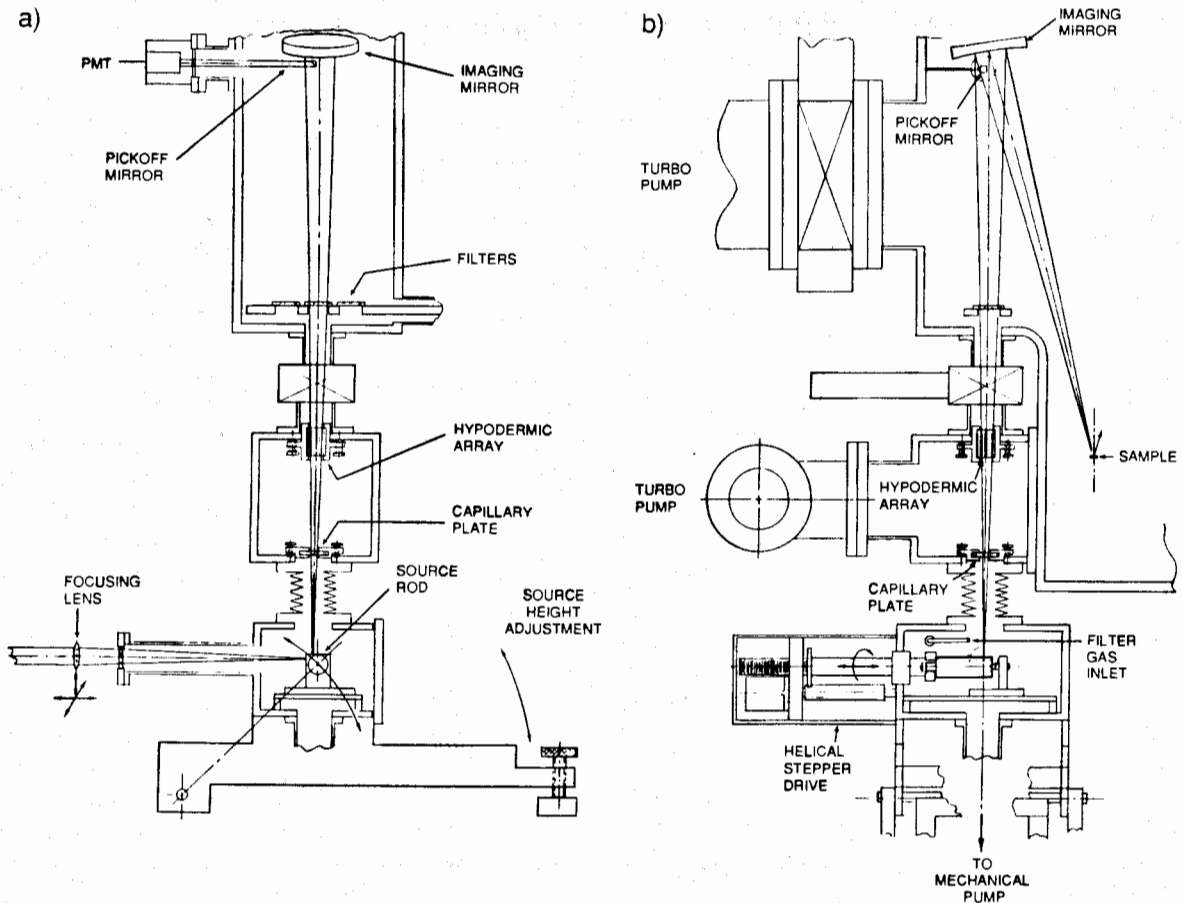


Fig. 2. Schematic representation of the Laser Plasma Light Source. (a) side view, (b) front view.

electrons, produces the strongest continuum radiation with minimal line output. The samarium continuum extends to approximately 400 nm with some lines visible in the emission in the 600 nm region. A typical spectrum of the LPLS from 5 to 40 eV is shown in Fig. 3, no attempt has been made to compensate for the response of the optical system. The LPLS produces a photon flux at the detector of approximately 500 photons/pulse/nm at 50 nm. To monitor the source intensity and stability a small "pick off" mirror prior to the main imaging mirror is used with a photomultiplier tube. This signal can be used for source normalization. The pulse to pulse stability of the laser determines the short term stability of the plasma output, while long term stability is determined by laser power drift and decrease in throughput arising from metallic deposition on the capillary plate. Deposition produces a decrease in LPLS intensity of  $\sim 20\%$  after  $10^7$  shots, a period of weeks.

## 2.2. Sample chamber

The light from the LPLS is order sorted using gas-phase and solid-state filters. The diverging light from the plasma is then collected by a 3 inch diameter Ir coated spherical mirror. Other light sources, such as deuterium or tungsten lamps can also be used in this system. The light is focused, with 1.25:1 imaging, off of the reference mirror or sample onto the 100  $\mu\text{m}$  entrance slit of the polychromator. The  $f$  number of the complete optical system is 40 and maintained by apertures in the reflectometer and polychromator. The illuminated area on the sample is 2.5 mm in diameter, and can be further reduced for smaller samples by apertures.

Sample positioning is one of the critical aspects of the

system performance. Five samples can be measured in the reflectometer with out breaking vacuum. Standard sample size is 1 cm diameter discs, 400  $\mu\text{m}$  in thickness, but samples of arbitrary dimensions are easily measured. Reflectance samples are mounted horizontally on sapphire tripod stands which are placed on a kinematic goniometer by an *in situ* sample transfer system. For proper imaging of the plasma

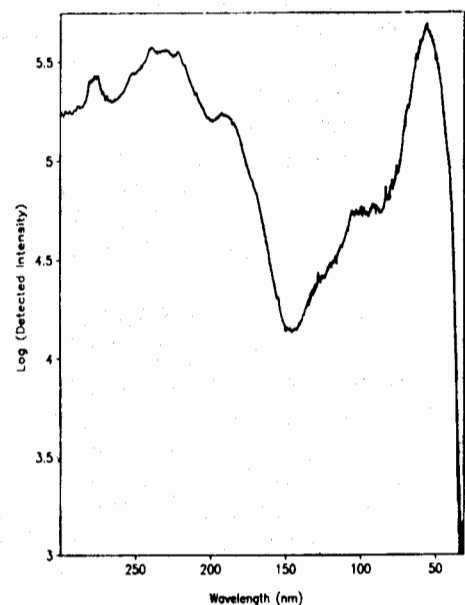


Fig. 3. Detected intensity spectrum of the LPLS, with detector dark current subtracted. The output of the LPLS is a broad band continuum, with no line output in this energy range, the structure in the spectra arises due to iridium optics used and the overall spectrophotometer efficiency.

light, the sample must be positioned by the goniometer at the correct angle to maximize the light into the entrance slit. At the same time sample height must produce the correct path length for formation of the plasma image on the entrance slit, and the sample must be centered in the optical path. The tripod stands adjust the height and tilt of the sample to compensate for the sample thickness and center the sample in the optical path. This sample alignment is accomplished by mounting the tripod stand and sample on an external jig on a granite surface plate, and indicating, prior to installation, the correct sample positioning. Coupled with the goniometer tilts, this procedure assures positioning of the sample in the optical path. Two reference mirrors can be placed in the sample position independent of the goniometer for incident intensity determination and also serve for cross checking mirrors *in situ*. Transmission measurements are performed using a reference mirror and introducing one of the two sapphire tripod mounted transmission samples between the reference mirror and the entrance slit.

Sample heating is by a 150 Watt, 10.6  $\mu\text{m}$  cw  $\text{CO}_2$  laser which is incident on the tripod mounted reflectance and transmission samples. The  $\text{CO}_2$  laser beam enters and exits the spectrophotometer by Indium sealed ZnSe windows and only crosses the VUV optical plane at the sample position. The laser beam exits the system before entering a water cooled beam dump. A shutter in the optical path simultaneously obstructs both the imaging mirror and the entrance slit, to minimize the contamination of optics by vaporization from hot samples. Samples can be heated *in situ* during a VUV measurement to temperatures in excess of 2300 K.

VUV spectroscopy at high temperature requires methods to discriminate the black body from the incident radiation to assure a suitable signal to noise ratio. The dispersive nature of the detection serves to discriminate the black body from the incident LPLS radiation. Spectra acquired from samples at 1800 K show no degradation in the signal to noise ratio relative to room temperature. Spectra at significantly higher temperatures can be taken by direct measurement of the black body radiation signals at the detector during the period between laser plasma pulses. Sample temperatures are measured by combined use of thermocouples embedded inside the samples and optical and infra-red pyrometry.

Low temperature reflectance and transmission measurements are performed using a flowing He cryostat which is horizontally mounted on a UHV manipulator with six degrees of freedom ( $x$ ,  $y$ ,  $z$ , rotation, two tilts) allowing sample positioning in either the reflectance or transmission position.

### 2.3. Polychromator

The polychromator is a 1-m, modified Rowland Circle instrument with two indexable gratings, an 1800 groove Ir coated ruled grating for high resolution high energy spectra, and a 600 groove Al/MgF<sub>2</sub> grating for wide coverage, low energy spectra. A diverter mirror and additional slit is provided on the exit slit path to permit a HeNe laser beam to be introduced into the VUV optical path to aide in alignment of the system.

### 2.4. Detection

The dispersive detector is a gated, intensified 1024 element reticon detector. A sodium salicylate phosphor is deposited

onto a curved focal plane fiber optic feedthrough inside the polychromator. This samples 5 cm of the focal plane, and is tapered to 2.5 cm outside of the system. The feedthrough is optically coupled to the fiber optic faceplate of the image intensifier which is then coupled to the reticon detector. The entrance slit of the polychromator is 100  $\mu\text{m}$ . The equivalent slit width of the detector is determined by the fiber diameter of the fiber optic feedthroughs, fiber misalignment at junctures, the pore diameter of the image intensifier, and blooming or cross talk among pores or diodes in the image intensifier and reticon. With 25  $\mu\text{m}$  fibers and diodes the 100  $\mu\text{m}$  entrance slit image will appear spread over 6 to 7 diodes. These combined effects lead to an effective exit slit width of 150–175  $\mu\text{m}$  for the detection system with the resulting spectra oversampled by 6 to 7 diodes. The system resolution therefore is 0.1 and 0.3 nm depending on grating, corresponding to an energy resolution of 3, 8 and 100 meV at 3.5, 10 and 35 eV respectively. The image intensifier can be gated synchronously with the LPLS to match the time duration of the high energy plasma light. At long wavelengths, into the ultraviolet, the plasma light persists out to approximately 400 ns. The optical multichannel analyzer can acquire up to 250 frames a second with 16 bit, 65000 count resolution. The overall detection system has nominal single-photon sensitivity.

The grating dispersion and detection allow collection of data in 23 or 70 nm wide spectral regions. Data taken from 5 to 40 eV involves acquiring 11 overlapping spectral regions. For good signal to noise ratio,  $2^{14}$  or  $2^{15}$  counts are acquired in each diode of the detector and requires 100–3000 shots of the LPLS. Acquisition of the incident and reflected spectra necessary to cover 5–40 eV takes 2 h.

Data from the optical multichannel analyzer are acquired on a 25 MHz 386 IBM compatible computer. Analysis of the spectra and calculation of the reflectance or transmission requires dark compensation and reference mirror compensation. The reflectivities are reproducible to 5%  $\Delta R/R$  or  $\pm 1\%$  in  $R$ . The adjacent spectral regions are chosen such that the overlap between regions serves to confirm the validity of the data. A complete reflectance spectrum from 5 to 40 eV contains 11 000 data points. No additional spectral smoothing is employed, the data presented here demonstrates the signal to noise ratio of the as collected data.

## 3. Some selected experimental results

The LPLS spectrophotometer gives us the capability to determine the electronic structure of ceramic materials at any temperature. In Fig. 4 we show the reflectivity of stoichiometric, man-made single crystal of  $\text{MgAl}_2\text{O}_4$ , an important ceramic material because of its structural relationship to MgO and  $\alpha\text{-Al}_2\text{O}_3$ . [10]. The data is presented as acquired, demonstrating the signal to noise ratio of a typical measurement. We can see the decrease of the reflectance to the expected value in the visible and asymptotically to zero at 40 eV. At 33 eV there is a small feature in the spectrum which corresponds to transitions from the O 2s lower valence band to the conduction bands, demonstrating that spectroscopy to 40 eV is required for these materials to encompass all of the valence interband transitions. The high temperature capabilities are shown in Fig. 5 where the  $\Gamma$  point exciton of single crystal MgO is shown as a function of temperature up to 1800 K. At this temperature the sample is glowing white hot, yet no

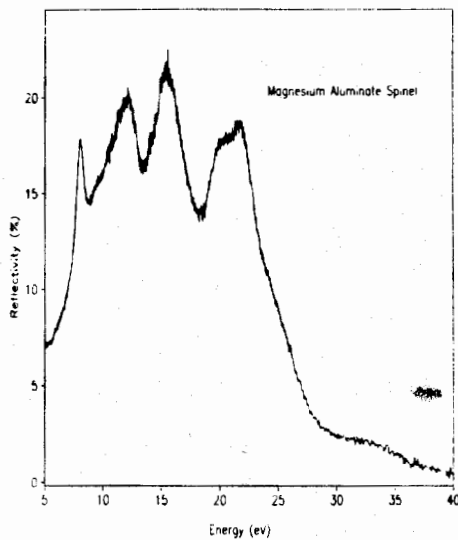


Fig. 4. Reflectivity of single crystal  $\text{MgAl}_2\text{O}_4$  at room temperature [9].

exceptional procedures have been used to recover the VUV reflectance from this sample. The exciton peak is seen to shift 1.4 eV to lower energies at a rate of  $-0.92 \text{ meV/K}$ , to broaden and to decrease in amplitude. These types of capabilities open horizons in our understanding of the high temperature properties of oxides.

### 3. Conclusions

We have developed a new vacuum ultraviolet spectrophotometer to measure the reflectance and transmission of solid samples from 1.7 to 40 eV (700 to 31 nm) with a resolution of 0.3 and 0.1 nm. This instrument uses a Laser Plasma Light

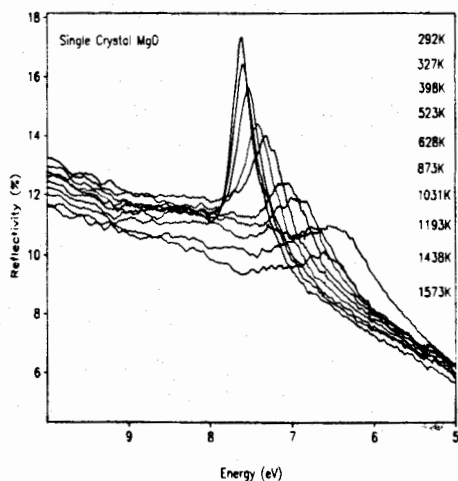


Fig. 5. Temperature dependence of the  $\Gamma_{15} \rightarrow \Gamma_1$  exciton peak in single crystal  $\text{MgO}$ .

Source with a samarium target to produce time-resolved high-brightness continuum radiation with good intensity, and positional stability. The instrument is of a single beam design, using a calibrated iridium reference mirror, with time-resolved dispersive detection leading to acquisition in 23 and 70 nm wide spectral regions. Acquisition of a spectrum over the complete energy range of the instrument is accomplished in 2 h. Measurements can be performed on samples heated by a  $\text{CO}_2$  laser to temperatures above 1800 K or cryogenically cooled to 15 K. The time resolution of the instrument is 20 to 400 ns. These capabilities in a laboratory based spectroscopy allow the determination of the electronic structure of materials at any temperature, with studies of the temperature dependence of the electronic structure, phase transformations and disorder to be addressed.

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