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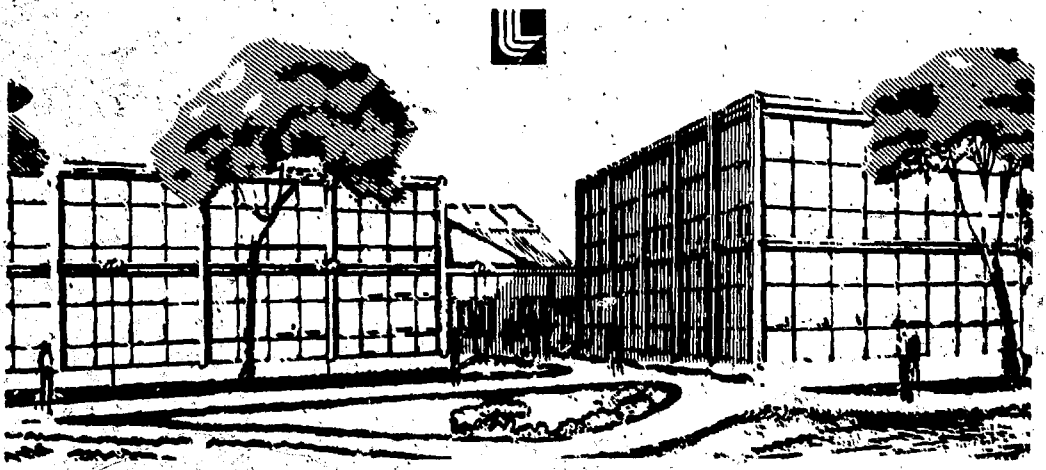

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RELAXATION OF NEODYMIUM IN A WEAKLY IONIZED EXPANDING PLASMA*

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ABSTRACT

The laser resonance absorption technique has been used to determine the relaxation rate of electronically excited neodymium vapor during its expansion into vacuum. Significant increases of population into ground and 1128 cm^{-1} levels were found. Analysis shows that interaction between excited metastable atoms and electrons are much more important for relaxation than atom-atom collisions. The final population of neodymium appears to be frozen at a temperature lower than the surface temperature of melt.

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I. INTRODUCTION

It is known that rapid expansion of gas may result in nonequilibrium between the translational, rotational, and vibrational degrees of freedom of the expanding gas.[1] During the expansion, a portion of energy might be removed from the translational modes by conversion to directed kinetic energy. For molecules with low lying vibrational and/or rotational energy levels, where rates for V → T and R → T energy transfer are in general fast equilibration among vibrational, rotational and translational degrees of freedom might be achieved in only a few or few tens of collisions. Considerable cooling of both the vibrational and the rotational temeprature of the molecule during expansion can be found.[2]

Little is known about the relaxation of the electronic temperature during gas expansion. For atoms with high lying electronic energy levels, coupling of electronic and translational energies is rather slow. The electronic temperature of atoms normally freezes early in the expansion. However, relaxation in a weakly ionized expanding plasma is a more complex problem. Since the exchange of electronic energy of atoms with kinetic energy of electrons can proceed rather rapidly, cooling of the electronic temperature might still be possible.

We report here some relaxation experiments on neodymium atomic vapor using a laser resonance absorption technique. It was found that the electronic temperature decrease rapidly during expansion. Simple analyses indicate that relaxation of low lying metastable states of neodymium probably results mainly from atom-electron collisions while atom-atom collisions are much less important. This information should be important to the development of efficient visible or UV laser systems with high pressure metal vapors.[3]

II. EXPERIMENTAL

The experimental system used in this work consists of three major components: atomic source generator, surface temperature and vaporization rate monitors, and CW laser-absorption apparatus. An overall schematic diagram of the system is given in Figure 1.

The atomic vapor is produced by surface evaporation of metallic neodymium by impact with high energy electrons. The electron beam is generated from a thermionic spot gun. Electron energy, current, and spot size of heating are continuously adjustable. A typical spot size is about 8 mm diameter. The electron beam strikes the sample surface at an angle of 24° from vertical. The debris produced by the primary beam consists of a swarm of electrons and ions together with excited and ground state atoms. The typical degree of ionization is about 10^{-3}.

Transient evaporation rates were monitored using a pair of quartz crystal deposition rate thin film monitors (TFM) located ~ 27 cm from the source at 0° and 14.5° from vertical. A metal collector was used to collect vapor emitted from the source. Averaged total evaporation rates were determined by measuring the target weight loss and weight gain of the collector, before and after the evaporation experiment. We found transient and average deposition rates measured by the two monitors were in good agreement with total vaporization rates assuming a cosine distribution.

Temperature measurements were made by sighting with an automatic optical pyrometer located directly above the source. The pyrometer was calibrated to the IPT's 1968 temperature scale by comparison with NBS reference lamp. Window absorption and emissivity correction factors were determined before the experiments.

The populations of neodymium atoms at the ground ($4f^4 6s^2$, J=4) and the 1128 cm^{-1} (J=5), 2367 cm^{-1} (J=6) and 3682 cm^{-1} (J=7) metastable levels [4] were determined by a laser resonance absorption technique. Figure 1 includes a schematic diagram of the optical setup. A Spectra Physics tunable dye laser is used for both line-width and percentage absorptiom measurements. The laser has a frequency bandwidth of about 30 MHz and an output power of 40 mW. The laser radiation is split into two beams. One is fed to a spectrum analyzer to monitor the laser bandwidth. The other beam is split again, 50% to a reference photodiode and 50% through the vapor chamber onto another photodiode. Neutral density filters were used for attenuation of the laser beam to avoid saturation or optical pumping effects. Signals from both diodes are then fed to a ratiometer and monitored on an oscilloscope and recorded on a chart recorder. During the evaporation experiment, the CW dye laser was tuned to sweep across the 5620 Å region for monitoring the ground state, 5676 Å for 1128 cm^{-1} and 5785 Å for 2367 cm^{-1} and 5827 Å for 3682 cm^{-1} levels. Line-widths and percentage absorptions for each transition were measured at various distances from the evaporation source. The absolute density of neodymium at each state was then calculated using published gA values.[5] Total particle density of neodymium at the absorption position was calculated from the flux and the average velocity. The flux was derived from quartz crystal deposition rate measurement and the calcualted velocity.

II. ANALYSIS

To evaluate the absolute density of neodymium at ground, 1128 cm^{-1}, 2367 cm^{-1}, and 3682 cm^{-1} levels, the relationship between absorptance and medium density was derived for a model where vapor expands from a spot source as shown in Figure 2. The general absorption equation can be written as:

$$\ln \left(\frac{I_o}{I}\right)_{W_L} = \int_{-x_o}^{x_o} \sigma_{W_L}(x)\, N(x)\, dx \qquad (1)$$

where the particle densities N(x), N(o) and the position of absorbing particles (x,y_o) are related by

$$N(x) = N(o)\frac{y_o^2}{x^2+y_o^2}\cos\theta = N(o)\frac{y_o^2}{x^2+y_o^2}\cdot\frac{y_o}{\sqrt{x^2+y_o^2}} \qquad (2)$$

Due to the horizontal velocity component and Doppler shift, the absorption cross sections $\sigma_{W_L}(x)$ and coordinates of absorbing particles are related by

$$\sigma_{W_L}(x) = \frac{\sigma_o}{\left[\frac{W_o - W_L(x)}{\eta/2}\right]^2 + 1} \qquad (3)$$

where σ_o is the peak absorption cross section at line center, η is the natural linewidth and $W_o = 2\pi\nu_o$. For particles traveling at a speed of

V, we have

$$W_L(X) = \left(1 \pm \frac{V}{C} \sin\Theta\right) W_o = \left(1 \pm \frac{V}{C} \frac{x}{\sqrt{x^2+y_o^2}}\right) W_o \tag{4}$$

Thus, the absorption cross section and medium density at position (x,y_o) can be written as

$$\sigma_{W_L}(X) = \sigma_o \frac{(x^2+y_o^2)}{\left[1+\left(\frac{2VW_o}{Cn}\right)^2\right] x^2 + y_o^2} \tag{5}$$

$$N(X) = N(o) \frac{y_o^3}{(x^2+y_o^2)^{3/2}} \tag{6}$$

Combining the above equations with (1), we get the following relations after integration from 0 to X_o,

$$\ell n \left(\frac{I_o}{I}\right)_{\text{at } W_L=W_o} = \frac{2N(o)\,\sigma_o y_o^3}{y_o^2 \left(\frac{2VW_o}{Cn}\right)} \tan^{-1} \frac{x_o \left(\frac{2VW_o}{Cn}\right)}{\sqrt{x_o^2+y_o^2}} \tag{7}$$

The quantity $\frac{2VW_o}{c\eta}$ is about 10^4, and therefore for any reasonable x_o and y_o values, we have the final expression for absorption from an expanding spot source:

$$\ell n \frac{I_o(W_o)}{I(W_o)} = \frac{\pi N(o)\sigma_o y_o}{\left(\frac{2VW_o}{C\eta}\right)} = \pi N(o) y_o \left(\frac{\sigma_o C\eta}{2VW_o}\right) \qquad (8)$$

Adopting the relationship $\sigma_L \Delta\nu_L = \sigma_o\eta$ and $\Delta\nu_L = 2\frac{V}{C}W_o$, we find:

$$N(o) = \frac{\ell n \frac{I_o(W_o)}{I(W_o)}}{\pi y_o \sigma_L} \qquad (9)$$

where $N(o)$ is the absorbent density at $\Theta = 0$ and y_o. Thus in principle by measuring $\Delta\nu_L$ and $\ell n \frac{I_o(W_o)}{I(W_o)}$ at known distance y_o from source, the absolute density of neodymium at ground, 1128 cm^{-1}, 2367 cm^{-1} and 3682 cm^{-1} can be determined.

The linewidth of atomic absorption due to Doppler broadening in a beam from an expanding spot source can also be derived as follows:

$$\nu_o \pm \frac{\Delta\nu_L}{2} = \frac{C \pm V \sin \Theta/2}{\lambda}$$

$$\Delta\nu_L = \frac{V \sin \Theta}{\lambda} = \frac{V}{\lambda} \frac{x_o}{\sqrt{x_o^2 + y_o^2}} \qquad (10)$$

where x_o is the optical pathlength of absorption and y_o is the vertical distance between the source and laser beam.

One can clearly see that at fixed evaporation conditions and distance y_o, the width of measured absorption should vary linearly with $x_o/\sqrt{x_o^2 + y_o^2}$, while the peak absorption $\ell n \frac{I_o}{I}$ at line center ν_o should remain constant for any reasonable x_o value. Since the spot size dimension (ν_o) is not very small compared to the observation distance (y_o), small deviations from the theory are expected.

IV. RESULTS

Equations (9) and (10) predict that the peak absorption depends only on vapor density at the intersection of the laser probe beam and vapor beam in the plane normal to the laser, and that the only effect of path length is on the linewidth. In order to test these predictions, absorption measurements were made for different path lengths at otherwise identical conditions.

The vapor beam from our source is collimated by the hearth so the path length at a position 3 cm. above the source is 8 cm. A tungsten mask was installed aboved the vapor source just under the laser beam to collimate the vapor stream intersected by the laser to 2 cm. During absorption measurements, the tungsten mask was pushed in or out of the vapor stream and absorption spectra were recorded for both positions. Figure 3 shows a typical set of absorption data. The top trace shows the signal observed in the absence of the tungsten mask. The bottom trace shows signal observed when the mask is in place. The top trace is clearly much broader. Due to the presence of the various isotopes naturally occuring in the neodymium sample: 27% ^{142}Nd, 12% ^{143}Nd, 24% ^{144}Nd, 8% ^{145}Nd, 17% ^{146}Nd, 6% ^{148}Nd, and 6% ^{150}Nd, the detailed structures of isotopes are not resolvable without the mask in place. However, when the tungsten mask is inserted, the absorption linewidth of each isotope was considerable reduced. The absorption profile of the even isotopes can be clearly identified. Because of their complex hyperfine structures, the spectra of odd isotopes are hardly recognizable. The ratio of total areas under the absorption profiles of the two experimental conditions was found to be about 3, in agreement with theory.

For the determination of the absolute population of neodymium in its various electronic levels, one requires the absolute absorption cross

section of the probed transition accurately, and the total particle density. Uncertainties in branching ratios and radiative lifetimes of reported transitions introduce a large uncertainty in the desired absolute populations. The total particle density of neodymium at the absorption position was determined from both evaporation rate and surface temperature data. As shown in Figure 2, the thin film monitor (TFM) located at y_{TFM} and $\Theta = 14.5°$ records the total particle flux (ground state, excited states and ions) from a source for the solid angle subtened by the detector. The relationship between TFM data and particle density at y_o, $\Theta = 0°$ can be written as

$$N_t\ (y_o,\ \Theta = 0) = \frac{\text{TFM Rate}}{\cos\ \Theta} \times \frac{1}{V} \times \left(\frac{y_{TFM}}{y_o}\right)^2 \qquad (11)$$

where V is the stream velocity of evaporant at y_{TFM} and y_o. The stream velocity can be calculated from

$$V_{Stream}^2 = \frac{2KT_o}{m}\ (1 + \frac{\gamma-1}{2}\ M^2\ )^{-1}\ \frac{\gamma M^2}{2} \qquad (12)$$

where γ is the heat capacity ratio of neodymium gas.

The relationship between the Mach numbers at two distances from the source is taken to be[6]

$$\frac{M_o}{M_{TFM}} = \left(\frac{y_o}{y_{TFM}}\right)^{2/3} \qquad (13)$$

and $M = 2(y_o/r_o)^{2/3}$, where y_o is the distance from the source and r_o is the source radius. Thus by measuring the surface temperature T_o, the stream velocity at y_o can be determined. The total particle density $N_t(y_o,0°)$ is then calculated from Eq. (11). Figure 4 shows the ratio of N_g/N_t employing Corliss's gA values[5] for 5620.54 Å. Using the published gA values for 5675.97 Å , 5784.96 Å and 5826.74 Å transitions, N_{1128}/N_t, N_{2367}/N_t and N_{3682}/N_t ratios were also determined.

The experimental data indicate significant increases in relative population during expansion for ground and 1128 cm^{-1} levels. There is very little change in population after $(y/r_o) > 6$. The final population of neodymium appears to be frozen at about 1600°K which is lower than the surface temperature of the melt. Due to uncertainties of absorption cross sections, the absolute populations shown in Figure 4 are only accurate to about ± 35%. Since the changes of relative populations is not affected by the absolute magnitude of absorption cross sections, our data clearly demonstrate that relaxation of electronically excited Nd atoms in a weakly ionized plasma proceeds very rapidly.

V. DISCUSSION AND CONCLUSION

As atoms evaporate from the liquid surface, they can be electronically excited by inelastic collisions by the high energy impinging electrons, expanding secondary electrons, and ions. Radiative lifetimes of most excited electronic states are very short[5], but since the branching ratios for cascading to the ground state are small, high populations in metastable excited states can build up after excitation. The relaxation of these metastable excited states during expansion can proceed by two different processes: a) relaxation by collisions with other neodymium atoms, or b) relaxation by collisions with the co-expanding electrons.

The relaxation of the excited state neodymium atoms by atom-atom collisions from an expanding spot source can be described by

$$\frac{Nd^m(y)}{Nd^m(r_o)} = \exp.\ \{ -\sigma_{E-T}\, Nd(r_o)\, \frac{r_o}{\gamma} [\ 1 - (\frac{r_o}{y})^{\gamma}\ ] \} \qquad (14)$$

where γ is the heat capacity ratio of neodymium gas and σ_{E-T} is the energy transfer cross section which is a function of kinetic temperature of the gas. For simplicity we have assumed it is roughly a constant. Figure 5 shows a plot of $Nd^m(y)/Nd^m(r_o)$ vs (y/r_o) for an initial vapor density at surface of 10^{15} atom/cm^3 and two distinct energy transfer cross sections. Cross sections for relaxation processes with ΔE = 1128 cm^{-1} and 3682 cm^{-1} were estimated from collective data[7] on alkali atoms. The spot radius, r_o and γ values were assumed to be 0.4 cm and 1.67 respectively. During the gas expansion, very little depopulation of 3682 cm^{-1} level due to E-T energy transfer is expected. However, collisional

relaxation of 1128 cm^{-1} to ground state or energy transfer between adjacent highly lying metastable states might still be possible.

As shown in Figure 5, heavy particle collisional relaxation ceases quite early at about $y = (2 \text{ or } 3)\ r_o$ for an initial vapor density of 10^{15} atom/cm^3. Thus further relaxation can only be achieved by other mechanisms, such as collisions with expanding electrons if their kinetic temperature is lower than the electronic temperature of the metastables. The two temperatures will essentially be de-coupled as the electron and neutral densities drop during expansion.

Since there are about 10^3 times more metastables than electrons in the vapor, cooling of the metastable-electon bath due to electron-electron collisions is probably slow. Furthermore the cross sections for superelastic collisions

$$Nd^m + e \xrightarrow{\text{de-ex}} Nd + e^* \qquad (15)$$

is too small for efficient relaxation of metastables at low electron densities. One possible relaxation process of Nd metastables can be described as follows:

$$Nd^m + e^* \xrightarrow{\sigma_{e\text{-}E}} Nd^* + e \longrightarrow Nd + h\nu \qquad (16)$$

where collisions between metastable Nd atom and electron excite the Nd atom into some nearby excited states of different parity. Since radiation from these states are optically allowed, relaxation of metastables by radiation can be accomplished.

Assuming that electrons retain constant kinetic energy as they expand into vacuum, the relaxation rate for Nd^m induced by electron metastable collisions can be calculated by

$$\frac{Nd^m(y)}{Nd^m(r_o)} = \exp\left\{-\sigma_{e-E}\, a\, Nd(r_o)\, \frac{V_{eo}}{V_d}\, r_o \left[1 - \left(\frac{r_o}{y}\right)\right]\right\} \qquad (17)$$

where a is the ratio of Nd^+/Nd which we have estimated to be about 10^{-3}, V_{eo} is the thermal velocity of electrons which is a function of average electron temperature, V_d is the directional velocity during expansion and σ_{e-E} is the excitation cross section of Nd due to electron impacts. For simplicity we have assumed it is roughly 10^{-15} cm^2. Similar values were found for other atomic transitions.[8] Figure 5 shows also a plot of $Nd^m(y)/Nd^m(r_o)$ vs (y/r_o) for initial vapor density of 10^{15} atom/cm^3 at an electron temperature of 1 eV. Note the collisions with low energy electrons in the expanding plasma might provide an effective channel for relaxation of neodymium metastables that result from electron impact excitation near the source.

The fact that increases of population in both ground and 1128 cm^{-1} levels were observed while little changes in either 2367 cm^{-1} and 3682 cm^{-1} were found (see Fig. 4) clearly indicates that relaxation of higher metastables (>0.5 eV), such as $4f^4 5d6s$ levels are involved. Since very little change in the populations of 2367 cm^{-1} and 3682 cm^{-1} were found, the feeding of these levels from higher levels must be as fast as its removing rates. It is clearly evident from our analysis that relaxation of high lying metastables (>0.5 eV) by collisions with other neodymium atoms through the E-T process freezes out quite early in expansion. E-T processes are partially responsible for the feeding of adjacent levels from nearby metastable states. Feeding of 1128 cm^{-1} and ground levels is most likely contributed from relaxations of high lying levels by collisions with low energy electrons followed by radiations.

In conclusion, a laser atomic absorption technique has been used to determine the transient population of neodymium atoms in vapor during an evaporation process. Here we have direct evidence that the electronic temperature of neodymium decreases during expansion. Theoretical analysis shows that interaction between excited metastable atoms and electrons are much more important for relaxation than heavy atom collisions. The final population temperature of Nd appears to be frozen at about 1600° K which is lower than the surface temperature of the melt.

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FIGURE CAPTIONS

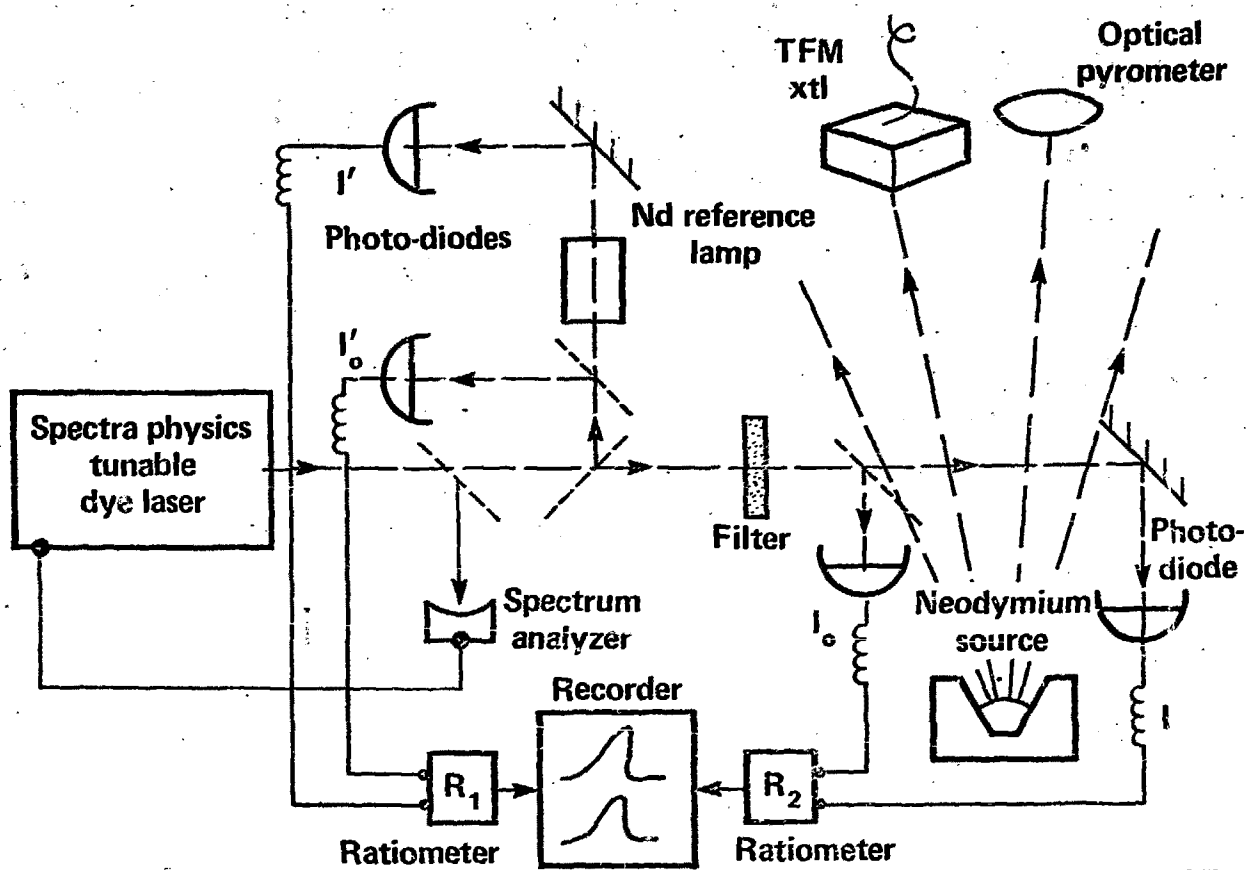
FIGURE 1 Apparatus for Atomic Absorption Experiment Using CW Dye Laser.

FIGURE 2 Geometry Used for Evaluation Of Atomic Absorption In An Expanding Spot Source.

FIGURE 3 Traces Of Atomic Absorption Signals Observed During the Evaporation Experiment. The CW Dye Laser Was Tuned To Sweep Across The 5620 Å Region For Monitoring Ground State Particle Density. Top Trace Shows The Signal Observed While The Tungsten Mask Is Out. Bottom Trace Shows Signal Observed While The Tungsten Mask Is In Place.

FIGURE 4 The Plot N_g/N_t, N_{1128}/N_t, N_{2367}/N_t and N_{3682}/N_t Observed at Various y/r_o During Expansion. The Source Temperature Was 1830°K. Due To The Uncertainties Of gA Values, The Data Do Not Give Accurate Information On The Absolute Population Of These States. The Absolute Values Are Accurate Only to About $\pm$ 35%.

FIGURE 5 Estimated Extent of Metastable Relaxations Induced a) By Collisions Between Metastables and Other Nd Atoms During Expansion $Nd^m + Nd \rightarrow Nd + Nd$. The Initial Source Density is 10^{15} atom/cm^3 and b) By Collisions Between Metastables And Low Energy Electrons During Expansion; $Nd^m + e^* \rightarrow Nd^* + e$ Followed by $Nd^* \rightarrow Nd + h\nu$. The Initial Source Density is 10^{15} atom/cm^3 and Degree of Ionization is 10^{-3}.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xtl
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pyrometer
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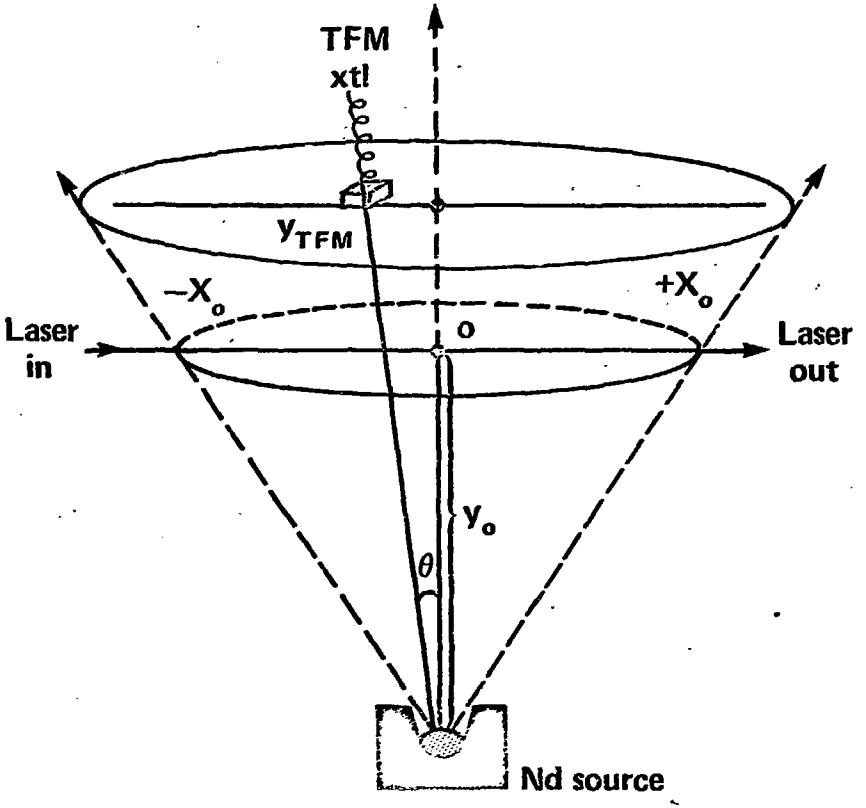

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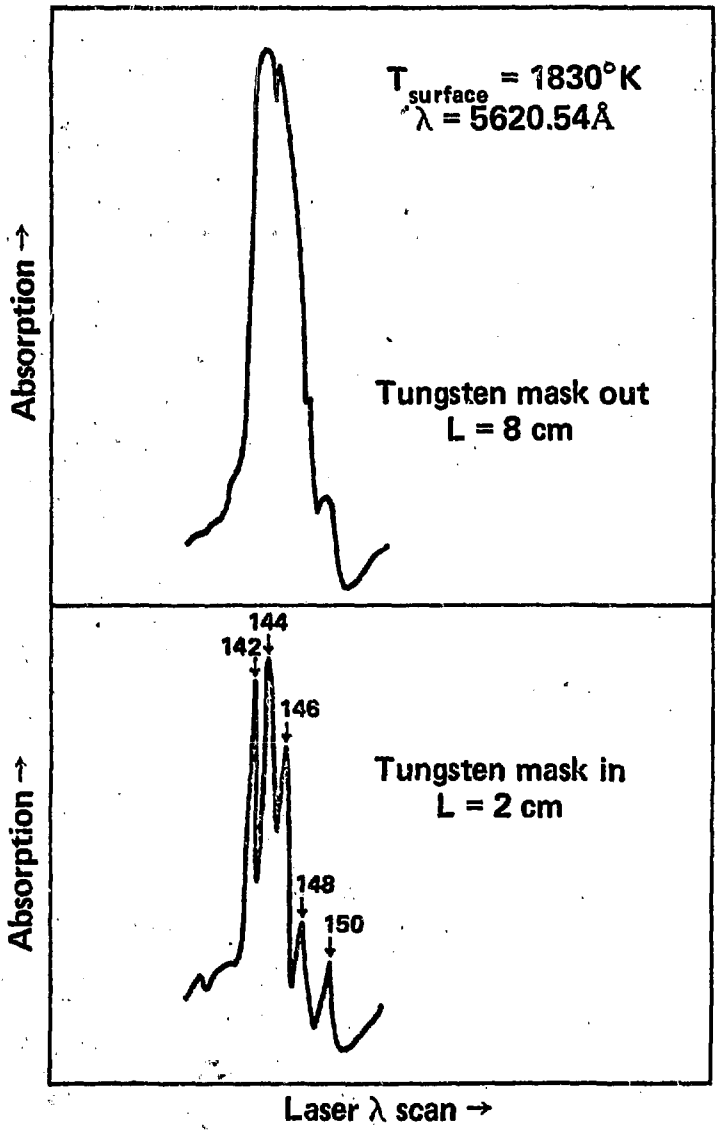
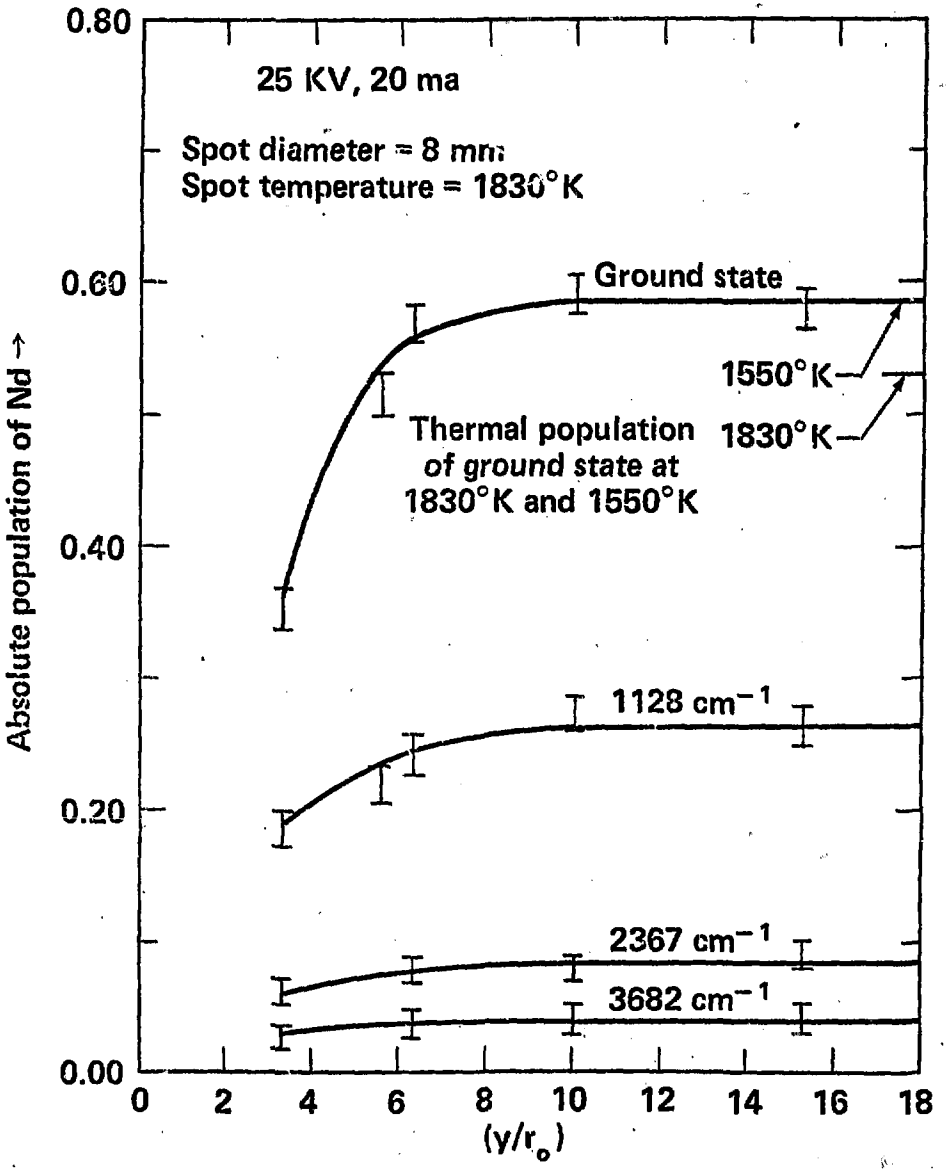
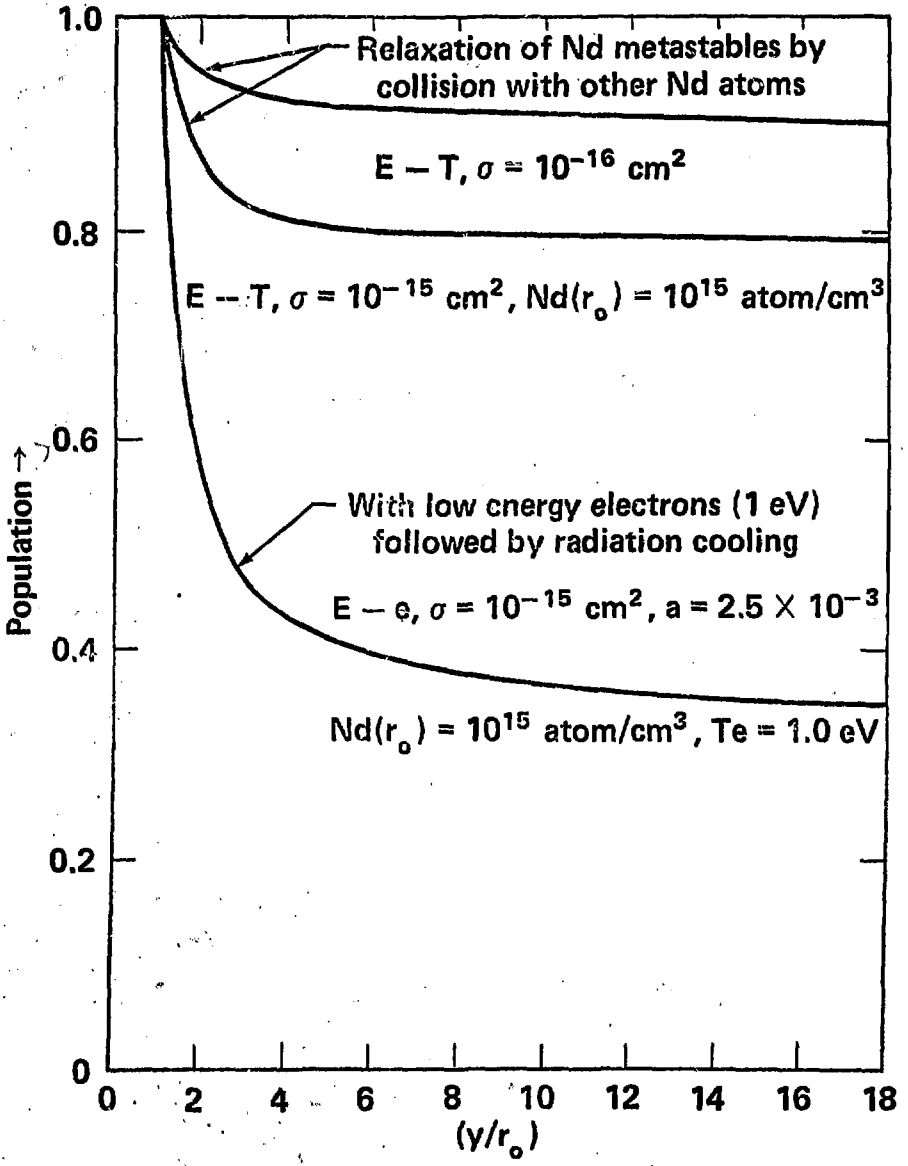

$T_{surface}$ = 1830°K
λ = 5620.54Å
Absorption →
Tungsten mask out
L = 8 cm
144
142
146
148
150
Absorption →
Tungsten mask in
L = 2 cm
Laser λ scan →


25 KV, 20 ma
Spot diameter = 8 mm
Spot temperature = 1830°K
Ground state
1550°K
1830°K
Thermal population of ground state at 1830°K and 1550°K
1128 cm⁻¹
2367 cm⁻¹
3682 cm⁻¹
Absolute population of Nd →
0.80
0.60
0.40
0.20
0.00
0
2
4
6
8
10
12
14
16
18
(y/r₀)


1.0
0.8
0.6
0.4
0.2
0
Population →
0
2
4
6
8
10
12
14
16
18
(y/r_o)
Relaxation of Nd metastables by collision with other Nd atoms
E — T, σ = 10^−16 cm^2
E — T, σ = 10^−15 cm^2, Nd(r_o) = 10^15 atom/cm^3
With low energy electrons (1 eV) followed by radiation cooling
E — e, σ = 10^−15 cm^2, a = 2.5 × 10^−3
Nd(r_o) = 10^15 atom/cm^3, Te = 1.0 eV