Laser spectroscopy of thulium atoms implanted in liquid and solid ^{4}He

Kiyoshi Ishikawa, Atsushi Hatakeyama, Koichi Gosyono-o, Shigeaki Wada, Yoshiro Takahashi, and Tsutomu Yabuzaki
Department of Physics, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan
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The excitation, emission spectra, and decay curves of the emission intensity of thulium atoms implanted in liquid and solid helium were observed in the presence and absence of an external magnetic field. The observed narrow line (width ~ 0.1 nm) of the excitation spectrum at 590.60 nm is assigned as a zero-phonon transition from the electronic ground state $4f^{13}(^2F^o_{7/2})6s^2$, which indicates that the transition between the inner shells is weakly perturbed by surrounding helium atoms. The pressure dependence of the emission wavelength suggests that the symmetry of helium atoms distributed around a thulium atom in the solid phase is similar to that in the liquid phase. The emission intensity was stable and large in the solid phase since thulium atoms were trapped at a density of 10^{10}–10^{11} atoms/cm^3. The lifetime of the excited state was measured to be 7.09 ± 0.04 μs, which was longer than that of the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ state of free thulium atoms. The excited state is expected to be a mixed state of the $4f^{12}5d6s^2$ and $4f^{13}6s6p$ configurations. The metastable state $4f^{13}(^2F^o_{5/2})6s^2$ is populated by a radiative transition from this excited state and relaxes to the ground state through a magnetic dipole transition. The lifetime of the metastable state of a neutral thulium atom was measured to be 75 ± 3 ms. [S0163-1829(97)00726-1]

I. INTRODUCTION

The excitation and emission spectra of foreign atoms in liquid helium are different from those of *free* atoms (hereafter the isolated atoms in vacuum are referred to as free atoms). The interaction of the valence electrons of such foreign atoms as alkali metal, alkaline-earth metal, and transition metal with surrounding helium atoms has been studied both theoretically[1,2] and experimentally by means of laser spectroscopy.[3–7] The magnitude of the interaction energy is typically of the order of the spin-orbit interaction of alkali metal atoms.[1] This is large enough to change the coupling case of angular momenta of the electronic state from that of a free atom. Generally the ground state and the optically excited state have different orbital angular momenta. Therefore the equilibrium distribution of helium atoms around the foreign atom differs for these states. This results in a broadening of the absorption line from the ground state and in the rapid nonradiative relaxation of excited atoms to a stable state.

We can observe not only foreign atoms but also helium atoms in liquid and solid phases through the excitation and emission spectra of foreign atoms obtained by laser spectroscopy. But optical excitation generally changes the distribution of helium atoms and releases large thermal energy, so that the atom whose valence electron is optically excited may not be a good probe to study the real properties of liquid (superfluid) and solid helium. If the atom interacting weakly with helium atoms is excited, less amount of thermal energy is released. Furthermore, if the excited and ground states have similar distributions of electrons interacting with helium atoms, the optical transition does not redistribute surrounding helium atoms. The inner shells ($4f$ and $5d$) of rare-earth metals are not filled with electrons, and so there are transitions between the inner shells. The electron of the inner shell is shielded by outer electrons[8] from large external perturbations. The line broadening and shift were reported to be small for the shielded transition of a thulium atom, one of the rare-earth metals, even in the pressurized helium gas.[9] The interaction between the excited electron and helium atoms is also expected to be small in liquid and solid helium.

In this paper, we report on a spectroscopic study of thulium atoms implanted in liquid and solid helium. The excitation, emission spectra, and the decay curves of the emission intensity were observed in the presence and absence of an external magnetic field. A very narrow excitation line at about 590 nm was observed both in liquid and solid phases, which was assigned as a zero-phonon line from the electronic ground state $4f^{13}(^2F^o_{7/2})6s^2$ (the same notation of energy levels as in Ref. 10). The full width at half maximum (FWHM) of this line was about 0.1 nm. This line was accompanied by a phonon sideband with a width of about 5 nm in the blue side. We could observe a magnetic dipole transition from the metastable $4f^{13}(^2F^o_{5/2})6s^2$ to ground state, and measured the lifetime to be about 75 ms in solid helium. Several works have been made on the properties of foreign atoms in the time region of milliseconds; one is the measurement of the lifetime of the magnesium metastable state[5] where the metastable state is produced by the recombination of magnesium ions and electrons after sputtering the bulk metal, and another work is the observation of magnetic resonance of the spin-polarized ground state of cesium atoms trapped in solid helium.[11] In this kind of study, one has to trap the atoms in a small spatial region during a long observation time. There are two well-known methods to trap microscopic particles in potential wells; charged particles can be trapped in an electromagnetic potential, and several species of neutral atoms can also be trapped by using the techniques of laser cooling and trapping. Such techniques cannot, however, be applied to neutral thulium atoms. The present experiment shows that solid helium is a good material to trap thulium atoms at the density of 10^{10}–10^{11} atoms/cm^3. In addition, we discuss the relaxation processes of the excited

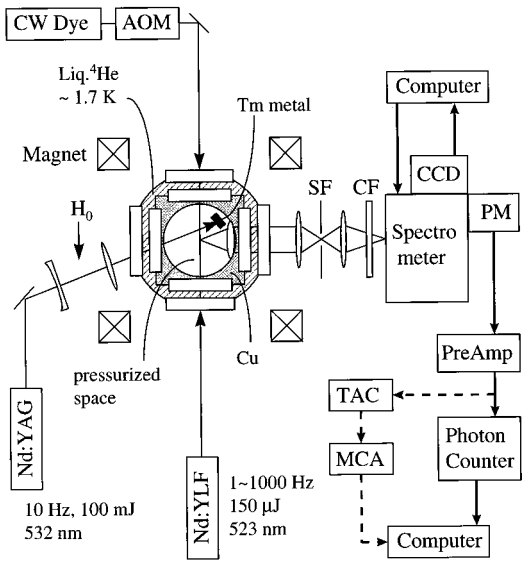

FIG. 1. Experimental setup. A bulk thulium metal is ablated with a Q-switched Nd:YAG laser at the repetition rate of 10 Hz, and clusters from the metal are sputtered with a Q-switched Nd:YLF laser at the repetition rate of 1–1000 Hz. The excitation beam and the second sputtering beam are propagated in the opposite direction to each other. The emitted light is corrected by a lens, transmitted through a spatial filter SF and a color filter CF, and detected with a visible or near-infrared sensitive photomultiplier PM and with a charge-coupled device CCD. Excitation pulses are produced with an acousto-optic modulator AOM from the cw output of a dye laser.

thulium atom in liquid and solid helium by using adiabatic potentials.

II. EXPERIMENT

The experimental setup is shown in Fig. 1. A piece of thulium metal was placed in a cell made of copper with four windows, the internal space of which was 22 mm in diameter and 40 mm in height. The cell could be pressurized up to 50 atm (1 atm $=101\,325$ Pa) and was inserted into the sample space of a cryostat (Oxford Instrument, Spectromag) where the quantity of liquid helium and its temperature were controlled with a needle valve and a heater. The temperature was kept constant at about 1.7 K. A magnetic field weaker than 3 T could be applied with a set of superconductor coils.

Thulium atoms were implanted into *liquid* helium by laser sputtering with two lasers, similarly to the case of alkali metals.[3] The vapor pressure of thulium is much lower than that of alkalis, so that a sputtering laser with higher pulse energy is required. The thulium metal was sputtered by the first pulsed laser of a Q-switched Nd:YAG laser (Lambda Physik, LPY150) with a pulse energy of about 100 mJ at a repetition rate of 10 Hz. The clusters ejected from the metal were sputtered by a second pulsed laser of a Q-switched Nd:YLF laser (Spectra-Physics, TFR) with a pulse energy of about 150 μJ and a repetition rate variable from 1 to 1000 Hz. New atoms were continuously supplied in *liquid* helium by these two pulsed lasers during the observation. Thulium atoms implanted in liquid helium were excited to two electronic states with a single-mode cw dye laser (Spectra-Physics, 380D) tuned to the wavelength regions of about 570 and 590 nm. The wavelength of the dye laser was calibrated with a wavemeter (Burleigh, WA1500) with absolute accuracy higher than 0.001 nm.

The implantation of thulium atom in *solid* helium was made by the following procedures. At first, the bulk thulium was ablated by the first pulsed laser at helium pressure slightly lower than 30 atm, at which helium was liquid during the ablation but crystallized in the absence of laser pulses. The first pulsed laser was repeatedly turned on and off until a thulium atom was implanted at sufficient density. The present method was similar to that in Ref. 4, except that in our case, after the implantation of thulium atoms and clusters into the solid helium was finished by the first pulsed laser, the pressure was raised to more than 35 atm which was high enough to make solid helium in a hexagonal-closed-packing (hcp) phase[12,13] (the highest pressure for a body-centered-cubic phase is about 30 atm). During the implantation by the first pulsed laser, the second pulsed laser and cw dye laser were applied to solid helium, in order to know roughly the number of implanted thulium atoms from the intensity of laser-induced fluorescence. These two laser beams were applied in the opposite direction to each other. The second pulsed laser was turned off when the spectra of thulium atoms in *solid* helium were observed.

The spontaneous emission in the wavelength region from 400 to 900 nm was detected with a charge-coupled device (CCD) (Prinston Instrument) cooled to about 170 K, through a spectrometer with 500 mm focal length. The emission spectra were obtained from two-dimensional data of the CCD with an integration time of about 1 s, while the excitation spectra were observed with a cooled visible-sensitive (VIS) photomultiplier (Hamamatsu, R943-02) and a gated photon counter (Stanford Research Systems, SR400). For the detection of emission in the infrared region between 900 and 1350 nm, we used a cooled near-infrared-sensitive (NIR) photomultiplier (Hamamatsu, R5509-41), connected to a gated photon counter. In *liquid* helium the emission intensity fluctuated shot by shot of the first and second sputtering lasers. On the other hand, the intensity fluctuation of emission was much smaller in *solid* helium because only the (cw) excitation dye laser was applied during observation. Furthermore, the emission in solid helium was much stronger due to the large concentration of thulium atoms, which enabled us to detect the change of the emission and excitation spectra by the changes of various parameters and helium conditions.

The decay curves of the emission intensity at 1140 nm, due to the transition between the $4f^{13}(^2F^o_{5/2})6s^2$ and $4f^{13}(^2F^o_{7/2})6s^2$ states, were obtained by using the NIR photomultiplier connected to a multichannel averager (Stanford Research Systems, SR430) which was operated in the photon-counting mode and piled up many counts in each excitation pulse. The excitation pulse with a width of 0.5 ms was produced by switching the cw dye laser with an acousto-optic modulator (AOM). For the detection of the emission decay in the visible region, we used a VIS photomultiplier and a correlated single-photon-counting system. In this case, the width and repetition rate of the excitation pulse were 50 ns and 10 kHz, respectively.

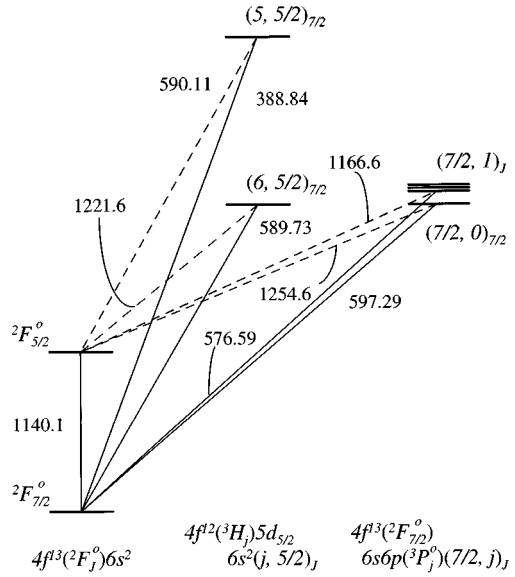

FIG. 2. A part of energy diagram of thulium atom isolated in vacuum, concerning observed spectra. The numbers are transition wavelengths in vacuum in units of nm.

III. RESULTS

In order to analyze the optical spectra of thulium atoms in liquid and solid helium, the wavelengths of observed lines are to be compared with those of free atoms. Figure 2 shows a part of the energy levels of free thulium atoms[10] together with transition wavelengths. The spectrum associated with the transition between the levels shielded by outer electrons is expected to be sharp even in liquid and solid helium. There are two such inner-shell transitions from the $^2F^o_{5/2}$ state and from the $^2F^o_{7/2}$ state, both in a wavelength region around 590 nm. Figure 3 shows typical emission spectra of thulium atoms in liquid and solid helium, obtained by tuning the excitation laser to 590.20 nm and 589.07 nm, respectively. The emission line in the solid phase is located at the blue side of that in the liquid phase. Figure 4(a) shows the observed pressure shift and broadening of the emission line seen in Fig. 3. In Fig. 4(a) we can see an apparent step in the shift at a helium pressure of around 27 atm. This discontinuity comes from the phase transition of helium at this pressure. An internuclear distance of helium crystal is exceedingly reduced by the external pressure because the volume of solid helium depends on the amplitude of the zero-point oscillation.[14] Figure 4(b) shows the dependence of the wavelength and width of the above emission line on the mean internuclear distance[12,15] between helium atoms, $R_{\mathrm{He-He}}$, estimated from the helium pressure. We see that both the line shift and broadening have nearly linear dependence on $R_{\mathrm{He-He}}$, whatever the helium phase is. In addition, the emission line shape of thulium atoms in solid helium is about the same as that in liquid helium, so that it can be considered that the nearest helium atoms contributing dominantly to the shift and broadening are distributed similarly around a thu-

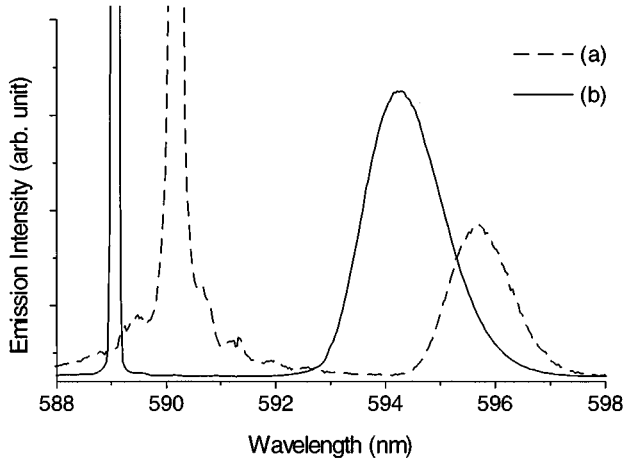

FIG. 3. Emission spectra of thulium atoms (a) in liquid helium at $P_{\mathrm{He}}=9.0$ atm and (b) in solid helium at $P_{\mathrm{He}}=35.6$ atm. In both cases, the temperature was fixed to about 1.7 K. Strong and sharp lines are laser lines tuned to the peak of the excitation spectrum for the liquid phase, and slightly blue detuned from the peak of the excitation spectrum for the solid phase. The intensity of emission in the solid phase is much larger than that in the liquid phase.

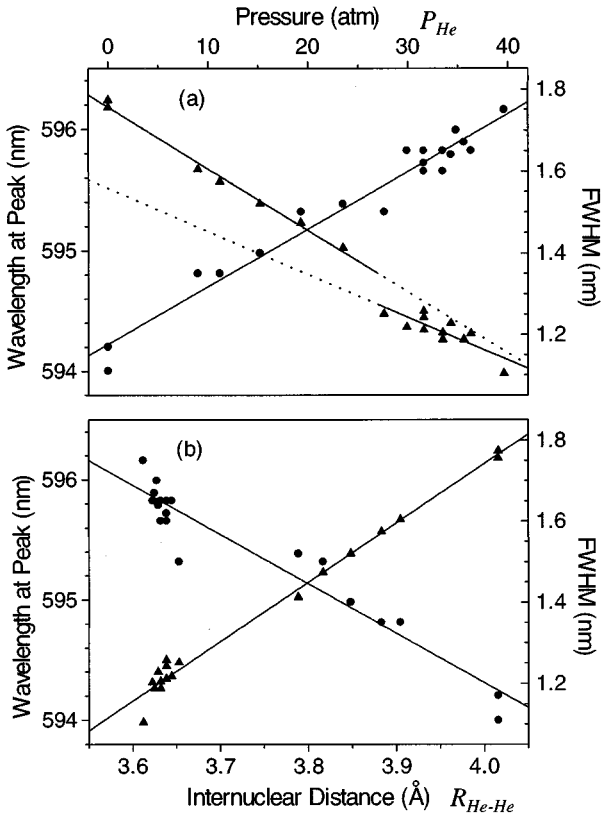

FIG. 4. (a) The pressure dependence of the wavelength at peak (triangles) and width (circles) of emission spectra shown in Fig. 3, at temperature of about 1.7 K. The power of the excitation laser was about 120 mW for liquid helium and 70 mW for solid helium. An apparent step in the shift of the wavelength can be seen at helium pressure of 27 atm. (b) The dependence of the wavelength at peak (triangles) and linewidth (circles) on the helium internuclear distance estimated from liquid density at 1.75 K (Ref. 12) and the molar volume at 0 K in the solid phase (Ref. 15) by using the relation $\frac{4}{3}\pi r^3 N_A = kV_m$, where r is internuclear distance, N_A the Avogadro constant, k the packing ratio, and V_m the molar volume. The value of k for the hcp phase is 0.74, which has been used in cases of both liquid and solid helium.

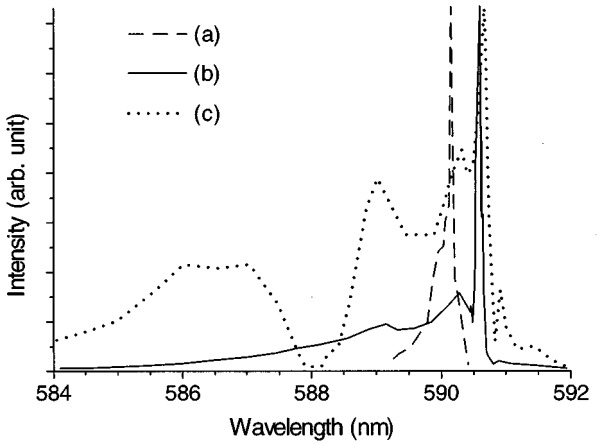

FIG. 5. Observed excitation spectra of thulium atoms in liquid and solid helium. The intensity of emission is normalized by the excitation power for each spectrum, but the relative intensities of (a), (b), and (c) are arbitrary. (a) shows the spectrum in the liquid helium at a saturated vapor pressure and at the temperature of 1.7 K. The monitored wavelength of emission was 596 nm. The power of the excitation laser was about 400 mW. (b) shows the spectrum in solid helium at $P_{\mathrm{He}}=34.8$ atm and the temperature of 1.7 K. The monitored wavelength was 594 nm. The excitation power was 1.8 mW and the counting rate was 5000 counts/s at peak intensity. The full width at half maximum of the narrow line in this spectrum is about 0.1 nm. (c) shows the spectrum in solid helium at $P_{\mathrm{He}}=39.8$ atm and the temperature of 1.7 K. The monitored wavelength was 1140 nm. The broad (width ~ 1.2 nm) dip at 588 nm may be due to the absorption from the $^2F^o_{5/2}$ state. The excitation power was 1.1 mW at the wavelength of 590.6 nm.

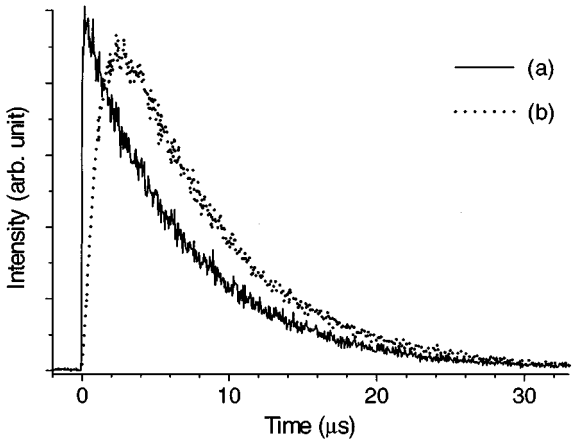

FIG. 6. The decay of the emission at 594 nm in solid helium. (a) shows the case that the wavelength of excitation was 590.57 nm. The excitation pulse was 50 ns in width and 0.4 mW at peak power. The helium pressure was 40.8 atm and the temperature was 1.7 K. The decay time was measured to be 7.09 ± 0.04 μs, which was independent of the helium pressure and the magnetic field intensity. (b) shows the case that the wavelength of excitation was 568.98 nm. The excitation pulse was 50 ns in width and 2.5 mW at peak power. The helium pressure was 41.6 atm and the temperature was 1.7 K. The rise time was about 1.1 μs and the decay time was the same as in the case of (a) within the fitting error.

lium atom, both in solid and liquid helium. Such a feature has been observed in the spectra of Cs and Ba atoms in liquid and solid helium,[2] although the spectra in these cases are due to the transitions of valence electrons. The phase transition of helium could be observed in the shift of the emission line; namely, we succeeded in probing one of the fundamental properties of a helium medium through foreign atoms. In order to probe thulium and helium atoms without heating effects, the implanted thulium atom was moderately excited by weak laser light in the following experiments.

Figure 5(a) shows the excitation spectrum in liquid helium, observed by detecting the intensity of emission at 596 nm. In Fig. 5(a) we see a narrow line located at the blue side of the emission line, the width being narrower than the emission line. The excited state will be named the $E1$ state hereafter. The corresponding excitation spectrum in solid helium is also shown in Fig. 5(b). The wavelength of the narrow line in solid helium is longer than that in liquid helium by 0.4 nm, and the FWHM is about 0.1 nm (3 cm^{-1}). We see a band at the blue side of this narrow line, which has not been observed in liquid helium. Judging from the shape of the spectrum in solid helium, the narrow line can be assigned to be a zero-phonon line which is homogeneously broadened and the broad band to be a phonon sideband.

The decay curves of the emission at about 594 nm were observed by exciting thulium atoms with a laser operated at about 590.6 nm, as changing the helium pressure P_{He} (in liquid and solid phases) and the magnetic field intensity H. A typical decay curve obtained is shown in Fig. 6(a), which is obtained in the case that $P_{\mathrm{He}}=40.8$ atm and $H=0$ T. The decay constant was measured to be 7.09 ± 0.04 μs for solid helium, which was found to be independent of P_{He} and H. This value is not so different from the averaged value of 7.13 μs in liquid helium. The radiative lifetimes have been measured so far for the electronic excited states of free thulium atom,[16,17] and the measured lifetime of the $4f^{12}(^3H_6)5d_{5/2}6s^2\ (6,5/2)_{7/2}$ state, which corresponds to the excited state in the present case, is 1.5 μs. It is important to notice that the state which gives the emission line at 594 nm is not an $E1$ state excited by the laser beam because the wavelength of the emission line is redshifted from the excitation line and because the zero-phonon line seen in the excitation spectrum has not been observed in the emission spectrum. Therefore we will call the emitting state the $E2$ state hereafter. It is considered from the measured decay constant that the $E2$ state is a mixed state of the $(6,5/2)_{7/2}$ state and some other state having a very long lifetime.

In the infrared region two emission lines were observed as shown in Fig. 7. The width of the emission line at 1241 nm was 5.5 nm (37 cm^{-1}), comparable to the width (49 cm^{-1}) of the emission line at 594 nm. Furthermore, the decay constant of emission at 1241 nm was measured to be about 7.1 μs, which agreed to that of emission at 594 nm within the limit of experimental errors. The above two facts indicate that both emissions at 1241 nm and at 594 nm originate from the common state $E2$, and that the line at 1241 nm is due to the transition to the $^2F^o_{5/2}$ state. Comparing with the transition wavelength of free thulium atoms, we see that the sharp line at 1140 nm in Fig. 7 is due to the magnetic dipole transition from the $^2F^o_{5/2}$ to $^2F^o_{7/2}$ states. The integrated intensity of this line is not so different from that of the line at 1241 nm, which implies the fact that the radiative transition is only the channel of relaxation from the $^2F^o_{5/2}$ to $^2F^o_{7/2}$

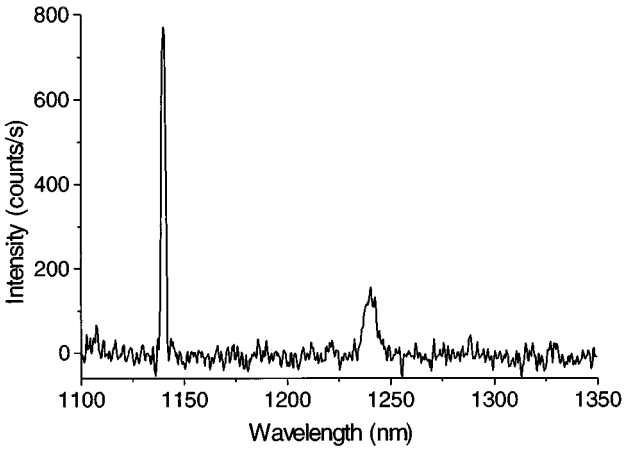

FIG. 7. The NIR emission spectrum of thulium atoms in solid helium at $P_{\mathrm{He}}=40.4$ atm and at the temperature of 1.7 K. The excitation wavelength and power were 590.57 nm and 1.4 mW, respectively. The line at 1241 nm is due to the transition from the electronic excited state $E2$ to the $^2F^o_{5/2}$ state. The line at 1140 nm is due to the transition between the $^2F^o_{5/2}$ and $^2F^o_{7/2}$ states.

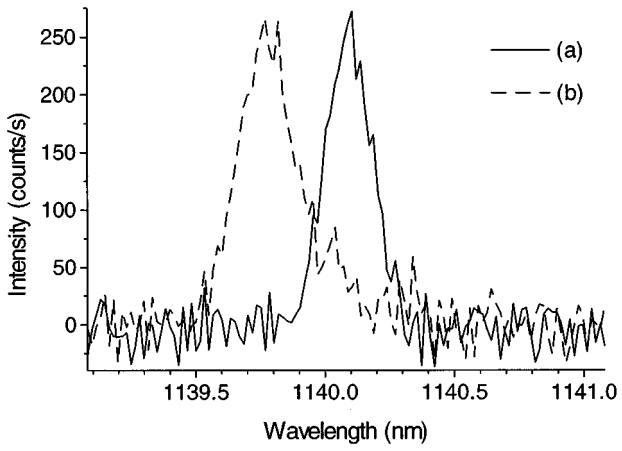

FIG. 8. The emission spectra due to the $^2F^o_{5/2}$-$^2F^o_{7/2}$ transition of thulium atoms in solid helium (a) without an external magnetic field and (b) with a magnetic field of 3 T. The excitation laser with the power of 2.0 mW was tuned to 590.57 nm in both cases. The spectral resolution was 0.2 nm which was determined by the slit width of the spectrometer. The line is shifted to higher energy with slight broadening in the magnetic field. The magnitude of shift is nearly equal to the difference between the shifts of sublevels, $^2F^o_{5/2}$ ($m_J=-5/2$) and $^2F^o_{7/2}$ ($m_J=-7/2$), and the broadening is due to the transitions between the $^2F^o_{5/2}$ ($m_J=-5/2$) and $^2F^o_{7/2}$ ($m_J=-3/2,-5/2$) levels. The wavelength of the corresponding transition of free thulium atoms is 1140.09 nm.

states. There is a relation among the wave numbers of the three emission lines; the wave number 16 829 cm^{-1} (594.2 nm) is nearly equal to the sum of 8059 cm^{-1} (1241 nm) and 8771 cm^{-1} (1140 nm). In addition, as mentioned later, the observed wavelength 1140.1 nm of the magnetic dipole transition coincides well with that of free atoms within the resolution of the spectrometer. These facts suggest that the potential curves of the $^2F^o_{5/2}$ and $^2F^o_{7/2}$ states are almost parallel to each other in a relatively wide range of configuration coordinates; i.e., both states are subjected to about the same perturbation by surrounding helium because of the same electronic configuration.

Figure 8(a) shows the emission spectrum for the $^2F^o_{5/2}$ to $^2F^o_{7/2}$ transition in solid helium which has been obtained with a resolution (0.2 nm) one order of magnitude higher than that for the spectrum shown in Fig. 7. The linewidth shown in Fig. 8(a) is still instrumental. It must be emphasized that the wavelength at the peak of this spectrum coincides with that of the free atom within an error less than the above resolution. In this way, we found that the shielding by outer electrons is more effective in this transition than in the $5d$-$4f$ transition. The effect of the external magnetic field of 3 T on the above-mentioned line is shown in Fig. 8(b), where we see that the line is shifted to higher energy with slight broadening. The magnitude of the shift is nearly equal to the difference between the shifts of sublevels, $^2F^o_{5/2}$ ($m_J=-5/2$) and $^2F^o_{7/2}$ ($m_J=-7/2$), calculated with g values of thulium atoms in vacuum, and the broadening is due to the transitions between the $^2F^o_{5/2}$ ($m_J=-5/2$) and $^2F^o_{7/2}$ ($m_J=-3/2,-5/2$) levels. This indicates that relaxation occurs in the $^2F^o_{5/2}$ state to the lowest-energy sublevel within the lifetime of this state.

Figure 9 shows the decay of the emission intensity due to the transition from the $^2F^o_{5/2}$ to $^2F^o_{7/2}$ state, which can be observed only in solid helium, and not in liquid helium because the decay constant is longer than the transit time of thulium atoms in liquid helium. The decay constant was measured to be 75 ± 3 ms by fitting a single exponential function to the tail of the curve. But the measured decay constant increases with the increase of helium pressure. This pressure dependence is rather curious because higher pressure causes generally larger perturbation of the surrounding helium, resulting in faster decay. Therefore we conclude, at the present stage, that the pressure dependence of the lifetime is treated as an uncertainty of 3 ms. In order to measure the decay constant more accurately, we need to observe the decay curves many times, taking account of the following discussion.

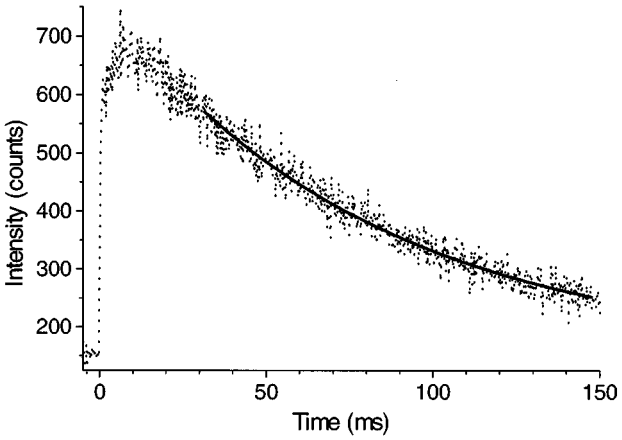

FIG. 9. The decay curve of emission due to the $^2F^o_{5/2}$-$^2F^o_{7/2}$ transition of thulium atoms in solid helium at the pressure of 39.7 atm and at the temperature of 1.7 K. The solid line shows the best-fitted curve. The decay time was 75 ± 3 ms. The width of the excitation pulse was 0.5 ms at a 1 Hz repetition rate, the peak power 19 mW, and the wavelength 590.57 nm.

At the present stage, we do not know how much the lifetime of the metastable state $^2F^o_{5/2}$ of free atoms deviates from the measured decay constant in solid helium. Let us consider briefly the possible causes of the deviation. The first one is the mixing of some other state to the $^2F^o_{5/2}$ state. The metastable state is isolated in energy from the ground and other excited states. So the state mixing by surrounding helium can be expected to be small, as we have seen in the excellent coincidence of the wavelengths of the magnetic dipole transition $^2F^o_{5/2}$-$^2F^o_{7/2}$ in solid helium and in vacuum. To study this in detail, we have to change the helium pressure in a wider range. The second possible cause is the disappearance of thulium atoms from the observed area by diffusion. The emission from thulium atoms trapped in solid helium had been observed without sputtering for 1 h. The time constant of disappearance is too long to shorten the emission decay. The third is the disappearance by clustering of thulium atoms. The emission intensity became large by irradiation of the second sputtering laser with the first pulsed laser remaining to be turned off. The emission intensity decayed quickly and became stable soon after the last sputtering pulse. The fast decay might be due to the clustering of thulium atoms created at a position nearby each other. The number density of thulium atoms after the fast decay of emission is calculated to be 10^{10}–10^{11} atoms/cm^3. Most of the atoms are found to stay in the $^2F^o_{5/2}$ state by solving the four-level ($^2F^o_{7/2}$, $^2F^o_{5/2}$, $E1$, and $E2$) rate equation based on the observed emission intensity, the measured decay constants for emission at 1140 and 594 nm, and the excitation efficiency at 590.60 nm. Therefore the average distances between thulium atoms seem to be too large to interact with each other. We should study the clustering mechanism of thulium atoms in the ground and/or excited states by concentrating thulium atoms in helium crystal in as high a density as possible.

In the excitation spectrum shown in Fig. 5(c), which was observed by monitoring the emission at 1140 nm, we can see a relatively large phonon sideband and a broad dip at 588 nm. Since the wavelength of the dip is close to that for the transition from the $^2F^o_{5/2}$ to $4f^{12}(^3H_5)5d_{5/2}6s^2$ $(5,5/2)_{7/2}$ states of free thulium atoms, we believe that the broad dip is due to the reexcitation from the $^2F^o_{5/2}$ state to the $4f^{12}(^3H_5)5d_{5/2}6s^2$ $(5,5/2)_{7/2}$ state, which is an inner-shell transition. Although we could not observe a direct transition from this upper state to the ground state, many relaxation paths including nonradiative processes are expected to exist in highly excited states.

Figure 10 shows the excitation spectrum in solid helium observed by monitoring the emission at 594 nm. Comparing with the line in Fig. 5(b) we see that the excitation line in Fig. 10 is considerably broad, although both lines are due to the excitation from the common ground state. When thulium atoms were excited through this line, the emission except for 594 nm could not be observed with our CCD system. We observed also the decay of the emission at 594 nm, and the result is shown in Fig. 6(b). The decay constant was measured to be 7.06 μs, which was in good agreement with that of the decay curve shown in Fig. 6(a). The excited state (named $E3$) is expected from the level energy[10] to be primarily the $4f^{13}(^2F^o_{7/2})6s6p(^3P^o_1)$ $(7/2,1)_J$ ($J=5/2$, 7/2, and/or 9/2) states. The rising time of the emission signal was 1.1 μs, which can be regarded as the time constant for the relaxation from $E3$ to $E2$ states under the assumption that this is the only channel of relaxation.

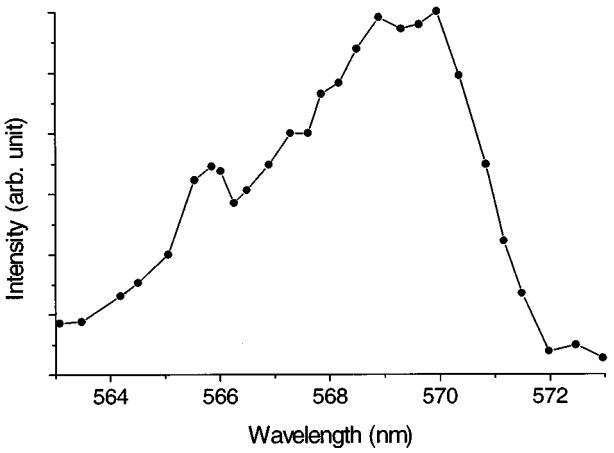

FIG. 10. The excitation spectrum of thulium atoms in solid helium at the pressure of 37.6 atm and at the temperature of 1.7 K, obtained by monitoring the emission intensity at 594 nm. The linewidth was about 4.6 nm. The spectrum was normalized by the excitation power which was about 1.8 mW at 570 nm.

IV. DISCUSSION

The excitation spectra of atoms in liquid and solid helium are generally broadened and shifted from those of free atoms because of the direct perturbation by surrounding helium atoms. The excitation line at 590 nm of thulium atoms is, however, extremely narrow. The linewidth is expected to be determined mainly by the natural lifetime of the excited states, because the related electron in the internal shell is shielded by outer electrons. The thulium atom is a many-electron system where, with respect to the angular momentum, only the total is conserved. Therefore, the complex coupling of angular momenta occurs in most electronic configurations. However, the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ and $4f^{13}(^2F^o_{7/2})6s6p(^3P^o_0)$ $(7/2,0)_{7/2}$ states can be considered to be almost pure states in this coupling scheme.[18] The electron densities for both states are spherically distributed within the orbitals of outer electrons, $6s^2$ and $6s6p$. The shift and broadening of absorption lines have been systematically analyzed for the thulium atom in the pressurized helium gas[9] and in solid neon.[19] In these works, the narrow lines were found to be due to the transitions between the inner shells. So we consider that the $E1$ state of thulium atoms in liquid and solid helium is mainly the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ state of free atoms. The lifetime of the excited state of thulium atoms in the solid neon matrix, which corresponds to the $E2$ state in liquid and solid helium, was reported to be 2.8 μs.[19] This is longer than the lifetime (1.5 μs) of the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ state of free atoms.[17] The lifetime of the $E2$ state in liquid and solid helium is 7.09 μs which is longer than any of those values mentioned above. Consequently, the $E2$ state is expected to be a mixed state of the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ state and the $4f^{13}(^2F^o_{7/2})6s6p(^3P^o_0)$ $(7/2,0)_{7/2}$ state, and the amplitude of the $(7/2,0)_{7/2}$ state in solid helium to be larger than

in the neon matrix. The lifetime of the $E2$ state is long because of the small electric dipole moment between the $4f^{13}(^2F^o_{7/2})6s6p(^3P^o_0)$ $(7/2,0)_{7/2}$ state and the ground state. The volume occupied by an atom in the neon crystal is larger than in the helium crystal. Therefore, the thulium atom by which a helium atom is replaced may be subjected to more stress from surrounding atoms than the thulium atom by which a neon atom is replaced. It can be considered that this difference in stress gives rise to the different mixing ratios of the $4f^{12}(^3H_6)5d_{5/2}6s^2$ $(6,5/2)_{7/2}$ and $4f^{13}(^2F^o_{7/2})6s6p(^3P^o_0)$ $(7/2,0)_{7/2}$ states.

The excitation spectrum shown in Fig. 5(b) consists of a zero-phonon line and a phonon sideband, both of which are apparently due to the excitation from the lowest vibrational level of the electronic ground state. Usually, the shape of the phonon sideband informs us of the shape of the upper and lower potential curves. In the present case, the observed phonon sideband distributes over 200 cm^{-1}, and so we see that the potential well of the excited state is deeper than 200 cm^{-1}. On the other hand, the energy of the zero-phonon line is the energy difference between the lowest vibrational levels of the excited and ground states. When we say ''zero-phonon line'' for the spectra of the impurity ions in crystals, it usually implies that the lattice is not excited through the zero-phonon transition. In solid helium, helium atoms are distributed in accordance with the electronic wave function of foreign atoms. Since the equilibrium distribution of helium for the excited state of thulium atoms is different from that for the ground state, helium atoms may move to their new equilibrium positions by the aid of the large amplitude of zero-point fluctuations. If we assume that the width of the zero-phonon line at 590.60 nm is given by the lifetime of the $E1$ state, helium atoms and electrons of foreign atoms must be redistributed within a time scale of 5 ps. This is consistent with the simple model that the redistribution time is of the order of $L/(d\nu)\sim 1/\nu\sim 0.6$ ps, where L is the displacement of helium atoms by the excitation of thulium atoms, and d and ν are, respectively, the amplitude and frequency of the zero-point oscillation. Because the actual line is broadened, more or less, by phase relaxation due to the helium perturbation, the lifetime is expected to be a little longer than 5 ps.

So far, the long lifetimes of metastable states have never been measured for the rare-earth metal atoms because of the difficulty to observe the same atoms for a long period of time. In the case of rare-earth ions, the spontaneous emission due to $4f$-$4f$ transitions has easily been detected, because many kinds of ions are implanted at high density in ionic crystal and that the emission intensity is strong. The lifetime is shortened by the electric field of crystal, which mixes the different parity states and allows electric dipole transitions. For example, the lifetime of the metastable state $4f^{13}$ $(^2F_{5/2}$-$E_{5/2})$ of Tm^{2+} was measured to be 6.5 ms in CaF_2 crystal.[20] In the present work, we could measure the decay time of the metastable state $^2F^o_{5/2}$ for neutral thulium atoms in solid helium, which was much longer than that of thulium ions in crystal. However, it is not clear at the present stage whether the measured decay time is intrinsic, as the lifetime of metastable state for free atoms, or determined by the external perturbations. As well as optical line shifts, widths, and decay times, the precise measurements of the hyperfine splittings of large-angular-momentum states ($^2F^o_{5/2}$ and $^2F^o_{7/2}$) and the magnetic relaxation times may provide information regarding the properties of foreign atoms in solid helium where foreign atoms are subjected to a large quantum fluctuation of helium atoms. We have shown that the relaxation between the sublevels of the $^2F^o_{5/2}$ state occurs within the lifetime, from the spectrum in a magnetic field of 3 T. It is also important to measure the relaxation time between hyperfine levels, which has been reported to be 0.6 ms for the ground state of thulium atoms in neon gas.[21]

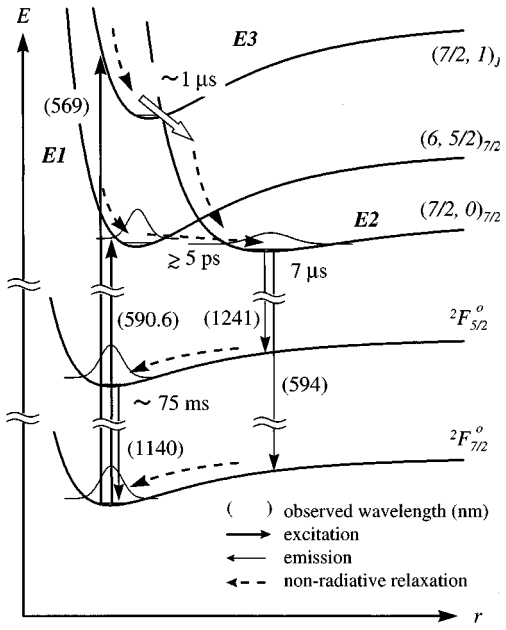

FIG. 11. The expected adiabatic potential curves of thulium atoms in solid helium in the spherically symmetric coordinate r. At a large value of r, each potential energy and the corresponding electron configuration approaches those of free atoms shown in Fig. 2. The potential curves of the $^2F^o_{7/2}$ and $^2F^o_{5/2}$ states are expected to have nearly the same shape because of the shielding of the spherically distributed outer electrons. The vibrationally excited atom in each electronic state relaxes rapidly to the lowest vibrational level. The lowest vibrational level of the $E1$ state relaxes to that of the $E2$ state. The rise time of the emission from the $E2$ state after the pulsed excitation to the $E3$ state was 1.1 μs, which corresponds to the characteristic time for the relaxation from the $E3$ state to the $E2$ state. It may not be a good approximation to express the potential curve of the $E3$ state in terms of the spherically symmetric coordinate because the outer electrons of the $E3$ state are not spherically distributed.

From the wavelength and width of the observed excitation and emission lines, we estimated roughly the adiabatic potential curves for the states in the present experiment, taking account of the measured decay rates. The results are summarized schematically in Fig. 11, where we also show the expected routes of relaxation. The potentials have been expressed one dimensionally in terms of a spherically symmetric coordinate. The pressure dependence of transition energy, shown in Fig. 4, indicates that the surrounding helium atoms around a thulium atom in the hcp phase of solid helium are distributed with similar symmetry as in the liquid phase. There are three reasons why a one-dimensional and spherically symmetric coordinate is a good approximation even in the hcp phase. At first, the outer electrons in both

$6s^2$ and $6s6p$ orbitals, which shield the inner electrons from the perturbation of surrounding helium atoms, are distributed spherically. Second, the number of nearest helium atoms around a thulium atom is expected to be larger than the number 12 of nearest neighbors in the pure hcp phase, and that is large enough for the electronic wave function to be insensitive to a fine deviation, from a sphere, of the distribution of nearest-neighboring helium atoms. The mass of ^{169}Tm atoms is much larger than that of ^{4}He, so that the amplitude of oscillation of thulium atoms is relatively small in solid helium. Finally, the zero-point fluctuation of helium atoms is large because of the small mass, so that helium atoms around a thulium atom can be considered to be distributed symmetrically according to the distribution of electrons in the $6s^2$ or $6s6p$ orbitals, rather than the stable sites in the hcp crystal.

V. CONCLUSION

In this paper we have reported on an observation of excitation and emission spectra of thulium atoms implanted in liquid and solid helium. The sharp excitation line at 590.60 nm in solid helium has been assigned as the zero-phonon transition between the electronic inner shells. The broadband at the blue side of the zero-phonon line is the phonon sideband in solid helium, while not observed in liquid helium. From the pressure dependence of the emission wavelength it was found that the surrounding helium atoms were spherically distributed around the thulium atom in either the excited state or the ground state, in liquid helium and even in solid helium of the hcp phase. The relaxation time for realignment of helium atoms accompanied by the excitation of thulium atoms has been estimated to be around or longer than 5 ps from the observed linewidth. The lifetime of the metastable state $^2F^o_{5/2}$ has been measured to be about 75 ms for thulium atoms trapped in solid helium. Thulium atoms, whose inner shell transitions are observed, offer an interesting subject to be studied not only from the viewpoint of atomic and molecular physics, but also from the point of view that they have a potentiality to be used as a probe or a tracer of liquid and solid helium because of a small perturbation to helium by optical detection.

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