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Terahertz electromagnetic transitions observed within the $^4I_{15/2}$ ground multiplet of Er$^{3+}$ ions in Si

S. Minissale,1 N. Q. Vinh,2 A. F. G. van der Meer,2 M. S. Bresler,3,* and T. Gregorkiewicz1

1Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands
2FOM Institute for Plasma Physics “Rijnhuizen,” NL-3430 BE Nieuwegein, The Netherlands
3A.F. Ioffe Physico-Technical Institute, RAS, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia

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The 30–300 μm wavelength range, which separates the predominantly optical and predominantly electric domains, is frequently referred to as the “terahertz gap” (1–10 THz). This reflects on the fact that the terahertz range remains poorly explored while almost the entire electromagnetic spectrum is exploited for practical applications, such as optical communications and data storage, spectroscopy, electronics and radiocommunications and telecommunications, radar, and x-ray diagnostics among others. The main reason for this situation is that to date no cheap and practical sources of terahertz radiation have been developed. In fundamental research concerning, e.g., carrier dynamics, the conveniently tunable free-electron lasers (FELs) remain the most popular radiation source. These installations are, however, highly impractical in view of their size and operational costs. Another solution is offered by optically pumped molecular lasers but these are also rather inconvenient with fixed emission wavelengths. At the same time, many interesting applications for terahertz range have been identified; these include remote sensing (molecule identification) and imaging for security and medical diagnostics, and also communications, where the terahertz band offers greater bandwidth and reduced antenna sizes. Therefore research toward development of a compact, versatile, and preferably electrically operated terahertz light source continues.1

In that context, a Si-based terahertz laser would be particularly welcome in view of the dominance of Si in contemporary electronics and the unprecedented sophistication of the Si complementary metal-oxide semiconductor (CMOS) technology. Here the possibility to use transitions between shallow donor and acceptor impurity states has been proposed,2 and stimulated emission from phosphor3 and arsenic4 donors in Si has been demonstrated. However these solutions require separate and powerful optical pumping (FEL and CO$_2$ laser in Refs. 3 and 4, respectively) and cryogenic temperatures. Therefore their projected applications are in space and atmospheric research rather than for the terrestrial concepts mentioned earlier. An alternative solution may be offered by quantum cascade lasers based on III-V compounds, which utilize intraband transitions,5 but operational temperature range of such devices is strongly hampered by polar-optical phonon scattering. This effect should be absent in Si (and Ge), which are nonpolar materials.6,7 Consequently concepts of cascade lasers based on (strained) Si-Ge quantum wells have been put forward8,9 and their realizations are being explored.10,11

Rare-earth (RE) ions are frequently used for tailoring optical properties of insulating and semiconducting hosts. For semiconductors, special attention has been given to Er doping of silicon, with the research clearly fuelled by prospect applications in Si photonics and optoelectronics—for a comprehensive review see, e.g., Ref. 12. RE-doped materials have also been considered for generation of terahertz radiation. At a time, it appeared plausible to use for that purpose optical transitions between individual levels within a single spin-orbit multiplet of a RE ion split by a local crystal field. This approach to terahertz generation turned out to be unsuccessful due to large width, and therefore mutual overlap, of emission lines from individual crystal-field-split levels. The situation is considerably different in Si/Si:Er multinanolayer structures grown by sublimation molecular beam epitaxy (MBE),13 where a single type of Er-related optical centers is preferentially formed.14–16 The low-temperature photoluminescence (PL) spectrum of this material features a set of very sharp lines with linewidth of $\Delta E<8\mu eV$. In this way, the major obstacle hampering previous attempts of utilizing Si:Er for development of a terahertz source has been removed. In this study, we explore the possibility of optical transitions between the well-defined crystal-field-split sublevels of the $^4I_{15/2}$ ground state of the Er$^{3+}$ ion in a Si/Si:Er multinanolayer structure.

The experiments have been performed on a Si:Er structure comprising 400 alternating Si and Si:Er layers—see Ref. 15 for sample details. As mentioned before, Er$^{3+}$ ions in this sample are preferentially incorporated in a single type of optically active center, designated Er-1, whose emission is characterized by ultranarrow emission lines. The ultrafast (picosecond resolution) pump-probe measurements in the terahertz range have been performed at the Dutch free-electron laser user facility FELIX. All the measurements were done at $T\approx 5\mathrm{~K}$ with the sample placed in a helium gas flow cryostat. The laser power incident on the sample was $P=50\mathrm{mW}$ [as measured at $\lambda_{\text{FEL}}=43\mu\text{m}$, 1 GHz repetition rate, and 7 μs (macro) pulse duration].
conclude that the lack of Er-related absorption band in the
FTIR spectrum cannot be seen as a decisive argument against
the existence of the investigated transition.

Consequently, we performed pump-probe experiments in
the $\lambda=43 \mu$m range of the expected transition. In these
measurements, an additional parameter appears—the lifetime
of the participating excited state. As mentioned before, for Er
we are dealing with a forbidden transition, while for B
the optical transitions are allowed. However in both cases
recombination transition probabilities are likely to be domi-
nated by nonradiative processes, as phonon scattering will
prevail over photon emission. On the other hand, we can
expect a considerable difference of the Huang-Rhys factor
for B and Er, resulting in different coupling to lattice
phonons. The experiment has been performed in the 
transient grating configuration. In this case, the FEL beam is
split into three parts by two polymer beam splitters (PP and
Mylar): two "pump" beams (having wave vectors $k_1$ and $k_2$)
and a "probe" beam, having wave vector $k_3$—see inset of
Fig. 2. The two pump beams are spatially and temporally
overlapped on the sample. Using a small angle of incidence
for the two pump beams and moving the sample up and
down, the grating can be "inserted" into the structure. In that
way the part of the sample closer to the surface can be se-
lected, thus reducing the substrate contribution and giving
advantage to the Er-doped top layer. Consequently, the Er-
related contribution relative to that of boron could be more
pronounced than in case of direct absorption. If the FEL is
resonant with an absorption transition available in the
sample, then the resulting excitation is spatially modulated
across the overlap region, resulting in a population grating.
The weaker beam $k_3$, spatially overlapped but time delayed,
is then Bragg diffracted off this grating into a phase-matched
signal direction ($k_3=\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_3$). By scanning the time delay

FIG. 1. (Color online) Schematic of the energy-level scheme for
the ground and the first-excited states of the Er-1 center. Gray zones
indicate energy range where additional thus far unidentified levels
should be located. Transitions observed in PL are shown by solid
arrows. Dotted arrows indicate possible terahertz transitions within
the ground-state multiplet; in red (dark gray), the $\lambda=43 \mu$m trans-
mission investigated in the current study is shown.

In the past, we have precisely determined the crystal-
field-induced splitting between sublevels of the ground state
of the Er-1 center.15 This is illustrated in Fig. 1, where also
the most prominent PL transitions used to establish this en-
ergistic scheme are indicated. On this basis, the wavelengths
of the possible terahertz transitions can be predicted. Identi-
fication of the $\lambda=43 \mu$m transition between the levels of
the $3^4I_{15/2}$ ground state of an Er$^{3+}$ ion—indicated in Fig. 1—is
the main subject of this report.

As an initial task, we carried out Fourier transform infra-
red (FTIR) absorption measurements on our sample in order
to demonstrate the presence of a linear absorption band at the
$\lambda=43 \mu$m wavelength of the predicted transition. Unfortu-
nately, no absorption signal has been detected, while the re-
liability of the experiment was assured by observation of an
absorption signal of $\approx 30\%$ and $\approx 65\%$, respectively, for the
two boron-related transitions at 40.8 and 35.9 $\mu$m. In order
to explain the negative result, we note that only $\approx 1\sim 1.5 \mu$m
of the total thickness of the sample contains Er, with a concentra-
tion of $N_{\text{Er}}=2 \times 10^{18}$ cm$^{-3}$, while B is present with a concentra-
tion of $N_{\text{B}}=2.7 \times 10^{15}$ cm$^{-3}$ in the $\sim 500\mu$m-thick substrate on
which the Si/Si:Er structure is grown. This implies that the areal density of Er
($N_{\text{Er}}=3 \times 10^{14}$ cm$^{-2}$) is of the same order as that of B
($N_{\text{B}}=1.3 \times 10^{14}$ cm$^{-2}$). At the same time, however, two fur-
ther corrections have to be taken into account: (i) the Er
transition is forbidden for parity reasons and its probability is
$10^2\sim 10^3$ times lower when compared to that of B and (ii) not
all Er dopants present in the sample will form the Er-1 center
and participate in the predicted absorption.17 Combining
these facts, we can expect the absorption by B to be consid-
erably ($\approx 2\sim 3$ orders of magnitude) stronger than by Er. By
inspecting the recorded linear absorption spectrum, we con-
clude that any Er-related absorption, if present, would be
below the background noise level and therefore impossible
to detect under conditions of the experiment. Therefore we
conclude that the lack of Er-related absorption band in the

FIG. 2. (Color online) Result of the pump-probe measurement at
$\lambda_{\text{FEL}}=43.5 \mu$m in transient grating configuration. A clear absorp-
tion band with a time constant of $\tau_{\text{F}}=52$ ps can be seen, superim-
posed on slowly decaying ($\tau_{\text{B}}=2$ ns) background, possibly of ther-
al origin. In the inset the interference pattern created on the
sample by the split pump beam is shown. The fringe separation $\Lambda$
depends on the wavelength and the angle between the pump beams
$\theta$: $\Lambda=\lambda/2 \sin(\theta/2)$.
The amplitude of the population grating can be measured as a function of time. The grating decays as $\exp(-2\tau/\tau)$, where $\tau$ corresponds to the time constant characteristic of the absorption transition generating the grating. In that way, the lifetime of the excited state can be measured. The transient grating technique has the important advantage of being practically background free; the diffracted signal appears only when the grating is formed due to absorption in the structure.\textsuperscript{18} In that way the appearance of any additional signals, not directly related to the investigated absorption, is avoided.

The pump-probe experiments performed in the transient grating configuration at the FEL wavelength of $\lambda=43.5$ $\mu$m revealed a clear absorption feature, as depicted in Fig. 2. From this measurement, the relevant decay time constant of $\tau=50 \pm 5$ ps was concluded. The slower, $\tau_2=2$ ns component observed simultaneously, represents most probably the heating effect, commonly seen in that configuration.\textsuperscript{19} Measurements performed at other wavelengths in that range (at 0.5 $\mu$m steps, not shown) yielded no absorption signal, thus evidencing the resonant character of the detected band.

The resonant aspect of the identified absorption band was further investigated in detail in a standard pump-probe reference configuration (see, e.g., Ref. 20 for experimental details). The results are shown in Fig. 3. In the main panel, the (normalized) traces for two wavelengths of $\lambda=43.5$ and 42.5 $\mu$m, i.e., "on" and "off" resonance, are compared. For $\lambda=43.5$ $\mu$m, the previously identified absorption band with $\tau$ (50 $\pm$ 5 ps) can again be seen. In that case, however, it appears superimposed on a faster decaying signal, characterized by a time constant of $\tau_F \approx 10$ ps. In the inset of Fig. 3, we show the wavelength dependence of the time constant dominating the absorption. As can be seen, the slow 52 ps component is indeed resonant, centered around $\lambda=43.5$ $\mu$m. A similar measurement performed on a B-doped Er-free sample did not reveal any resonances in that wavelength range. Consequently, we identify it with the expected ground-state transition of Er$^{3+}$. The origin of this fast component, which appeared in the whole investigated wavelength range and which was absent in the transient grating configuration, is not clear at this point and will not be considered further. For comparison, as for the FTIR absorption, we performed a similar experiment for the B-related band at $\lambda=40.8$ $\mu$m. A clear absorption with the characteristic decay time of $\tau=70$ ps (Ref. 21) has been observed. The amplitude of the B-related signal was approximately 50 times larger than that measured at $\lambda=43.5$ $\mu$m. This implies that the 43.5 $\mu$m band represents absorption of approximately 0.5%, too small to be disclosed in the FTIR measurement.

From the above presented experimental evidence we conclude that an optical transition within the $^1I_{15/2}$ ground state of the Er$^{3+}$ ion involved in the Er:Er center has been observed. We will now address the origin of the determined time constant. The theory of interaction of RE ions with lattice vibrations has been considered in the past. The lifetime of the upper (doublet) level is determined by spontaneous phonon emission,

$$\tau_p^{-1} = \frac{1}{\pi \hbar \nu} |\Phi_{nm'}| \frac{\omega^3}{\nu^3},$$

where $\omega$ is the frequency of the emitted phonon, given by the energy difference $\Delta E$ between the two states involved in the transition $\hbar \omega = \Delta E$. The matrix element of the RE ion-phonon interaction is determined by the matrix elements of Stevens operators,

$$\Phi_{nm'} = \sum_{m'0} (\chi_n A_{n0}^M)^2 |(Jm)| \langle O_{n0}^M |Jm'\rangle|^2.$$  

The constants $A_{n0}^M = g_n^M A_{n0}^0$ play the same role as deformation potentials in the theory of semiconductors—see Ref. 22 for the notation. Using also the values of the relevant quantities given in this reference, we can estimate the lifetime of the Er$^{3+}$ ion in the upper state of the ground multiplet as $\tau_p = 12 \times 10^{-12}$ s (where we have used the sound velocity averaged over three acoustic branches $\nu = 6 \times 10^5$ cm/s). We have included only the transitions from the upper-doublet-to-the-lowest-doublet state, since, as can be concluded from Eq. (1), the probabilities of the transitions to the closer doublets diminish as a cube of energy difference. We see that in spite of the very crude treatment, our result is of the same order as the experimental value of 50 ps.

The radiative lifetime for the transition from the upper to the lower doublet level is given by

$$\tau_{rp}^{-1} = \frac{\omega^3}{3 \pi \varepsilon_0 \hbar c},$$

where now $\omega$ is the frequency of the emitted photon (again given by the energy difference $\Delta E$), $\hbar$ is the Planck constant, $c$ is the light velocity, $\varepsilon_0$ is the dielectric constant of vacuum,
and $d_{12}$ is the dipole matrix element. We remark that the factor $\omega^2$ in Eq. (3) appears since the emission rate is proportional to the photon density of states ($\sim \omega^2$) but also to the square of the electric field of emitted light, i.e., to the photon stream ($\sim \omega$)—see, e.g., Ref. 23. Since the nonzero probability values for the $f \rightarrow f'$ radiation transitions are obtained only due to the admixture of $d$ states to the $f$ states of an Er$^{3+}$ ion, we can expect that the matrix elements are of the same order of magnitude for $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition and within the $^4I_{15/2}$ multiplet. Therefore, the difference in the radiation lifetimes for these transitions should be determined mainly by the photon density of states, i.e., by the cube of the ratio of the corresponding energies (equal to $\sim 30$). Consequently, assuming $\sim 10$ ms lifetime for the $^4I_{15/2}$ excited state of Er$^{3+}$, the radiative lifetime of the upper-doublet-to-lower-doublet transition can be estimated as $\tau = 10^{-3} \times 2.7 \times 10^7 = 270$ s. These estimates rule out the possibility of the experimentally measured lifetime being the radiative one; consequently, we identify it as being due to the nonradiative multiphonon recombination.

It is interesting to compare the current findings with the previously mentioned work on impurity level recombination of shallow dopants in silicon. In that case the relation between nonradiative and radiative recombination time constants is important. For Si:P, where realization of stimulated emission has been reported, the nonradiative recombination lifetime of $\sim 200$ ps has recently been measured. This value is in good agreement with the present finding. As for the radiative recombination, the exact value for P is not known, and values of up to $10^{-3}$ s have been reported. These values are considerably shorter than our estimate for Er, since the $1s \rightarrow 2p$ optical transition of P is allowed. On the other hand, the $f$ character of electronic functions involved in the Er transition could bring the advantage of a smaller linewidth; to this end we note that the width of the 2$p_0$ absorption band for Si:P (in an isotopically pure $^{28}$Si sample) has been established as $\Delta E = 4.2 \mu eV$, while for the Er transition only the upper limit of $\Delta E < 8 \mu eV$ is known at present, and a much smaller value of the linewidth can be expected.

In summary, the presented results conclusively identify an optically induced transition within the $^4I_{15/2}$ ground state of an Er$^{3+}$ ion in Si/Si:Er multilayer structure. The transition is observed in absorption at $\lambda = 43.5 \mu m$. At a liquid-helium temperature, the relevant relaxation lifetime is determined as $\tau = 50$ ps. We argue that this value reflects a nonradiative multiphonon recombination process. While past investigations of Si:Er have concerned the 1.5 $\mu m$ band relevant for telecommunications, the current result demonstrates that the nanoengineered Si:Er could also be relevant for the terahertz range. One attractive possibility could be to develop and explore plasmonic waveguides based on Si/Si:Er multilayer structures and in that way enhance the radiative recombination of Er$^{3+}$ ions, but for practical applications also ways to decrease nonradiative recombinations should be designed.

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11We point out that the number of Er dopants participating in the absorption band investigated here is likely to be (substantially) higher than the so-called “optically active” (Ref. 28) part [2–25% for the investigated structure (Ref. 29)].
12The transient grating will also appear due to the change in the refractive index, as a follow up of nonresonant effects involving virtual transitions. These, however, will exist only when the electromagnetic field is present, and therefore will reflect temporal characteristics of the laser pulse responsible for the generation of the transient grating.