ELECTRON-PHONON INTERACTION ON OPTICAL SPECTRA OF NANOELECTRONIC DEVICES

Quiesup Kim
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, USA

ABSTRACT

Using a simple long-wavelength phonon approximation theory, a phonon density of states is obtained. The temperature dependences of the widths of the zero-phonon lines and local mode were investigated using several phonon distributions including the effective density of phonon states obtained from the vibronic sideband. Low-frequency modes appear to make the dominant contribution to the broadening of the zero-phonon lines, whereas both low- and high-frequency phonons are active in broadening the local mode.

Experimentally, the low-energy vibronic sideband of the R lines of chromium at low temperatures was determined by the one-phonon and multi-phonon contributions to the observed spectral profile. The fluorescence spectrum of chromium-doped strontium titanate for example, was measured as a function of temperature. The one-phonon spectrum was found to be predominantly forced electric dipole in nature. Vibronic selection rules appropriate for such transitions were determined, and by comparison with neutron scattering and infrared absorption data could be identified with phase transitions of the material involving specific phonon (soft) modes more than 30 phonon peaks in the vibronic spectrum. Numerous low-frequency peaks are observed in the high-energy vibronic sideband, many of which cannot be associated with known vibrational phonon modes due to the higher order interaction among the electron-phonon interactions.

Based on the electron-phonon interaction, a technique utilized infrared excitation emission spectroscopy has been found to be useful for non-contact temperature measurement of a hot spot in 500nm-gate channel of a GaAs metal/semiconductor field effect transistor (MESFET). The technique was demonstrated on a powered and un-powered GaAs MESFET attaining a spatial resolution of 500nm. Precise knowledge of channel temperature of a GaAs device during operation is critical to determining the expected lifetime and overall device reliability.

Information obtained on the solid-state lattice dynamics by electron-phonon interaction between lattice phonons and electrons could open up to learn more about lattice dynamics and to apply it in nanoelectronic devices including software reliability, nano-size capacitors, master clock sources, as well as non-contact temperature probes on nano-electronic and photonic devices.

I. INTRODUCTION

Optical spectroscopy provides rapidly a means for mapping surface mineralogy in space. As an example, a reflectance absorption spectrum of a mixture of three common rock-forming minerals is shown below (Figure 1). Each mineral is a different molecule of minerals that absorbs energy in a region of the whole excited spectrum. From the spectrum the three minerals can be identified and with a radiative transfer analysis the relative concentrations of the minerals can be determined as shown in Figure 1.

Terrestrial materials have long served as analogs of the Martian surface, both chemically and spectrally. For example, the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) has sampled areas of California, Nevada, and Utah, having surface mineralogy that includes numerous clays, sulfates, iron oxides, carbonates and other minerals. The average terrestrial spectrum shows overall spectral shape and albedo level to similar spectra of Martian bright regions. Some areas containing hematite have visible spectrum that is very similar to the spectrum of Mars. The terrestrial spectra show strong clay absorption at 2.2 microns (-OH). The strength of comparable features (at 2.2 microns) in spectra of Mars are about a factor of 50 less, implying very low global abundance of OH-bearing materials with 2.2-microns absorptions. This implies a weathering history on Mars that differs substantially from that for Earth.
Several terrestrial minerals have been proposed as spectral analogs for Martian surface materials, and two groups in particular, the palagonites and the montmorillonites, have proven exceptionally popular. However, neither provides a perfect match to the observations, and the diagnostic 2.2-microns cat ion-OH vibrational absorption exhibited by most terrestrial clays has yet to be detected in spectra of the Martian surface. Mixtures of 5.0, 3.0, 1.0, and 0.5 weight % montmorillonite (SAz-1) in a spectrally bland basaltic powder having a 2.2-microns albedo similar to that of Mars have been measured. The Figure 2 shows the variation of band depth with clay content in the mixtures. For mixtures of as little as 5.0 weight % of clay, the 2.2-microns band is readily separated from the continuum, and is clearly distinguishable down to 1.0 weight %. Below 0.5 weight %, however, existing technology cannot achieve sufficient signal-to-noise to separate the 2.2-microns absorption from background. Between 5 to 0.5 weight % clay, band depths ranged from .013 to .0011 for the basalt-montmorillonite mixtures. Examination of the literature reveals that the upper limit to the 2.2-microns band depth for Martian spectra is 0.0007 micron (Clark, 1992, DPS Abstract), easily less than that for the 0.5 weight % clay mixture used in this study. This would imply that Martian soils of as much as 1 weight % clay can be ruled out on the basis of available spectroscopic data.\^\textsuperscript{1}

The amount of clay minerals on the surface of Mars is much lower than expected, less than two percent of that found on Earth. These low values may provide another clue to deciphering the mystery concerning the evolution of the surface and the potential for prior life on Mars. Clays may be important to the formation of life, perhaps as surfaces to which large molecules could stick. If clays never formed in abundance on Mars, life may not have been able to develop. If clays are being destroyed by some processes, then those processes might also have been hostile to the formation of life.

For decades scientists have debated the mineral composition of the Martian surface. Its red color was assumed to be caused by the presence of weathered iron oxides—also known as rust.\^\textsuperscript{1} Since iron oxides and clay are common products of the weathering process on Earth, they were assumed to be equally common on Mars. None of the spacecraft that have landed on Mars so far have been able to directly determine what minerals are present on Mars—though APX experiments have provided partial measurements of the underlying composition.

Mapping mineralogy is important to establishing the sequence of events which formed the present Martian surface. Particularly important is the identification of rocks and minerals formed in the presence of water since water appears to have played a dominant role in shaping the topography of Mars and is considered to be one of the key ingredients for formation of life. Current and past Mars missions have already sent back views of the Martian surface that seem to show evidence of dry riverbeds, flood plains, rare gullies on Martian cliffs and crater walls, and sedimentary deposits that suggest the presence of water at some point in the history of Mars.

The current body of evidence for these structures arises largely from interpretations of albedo (and scattering) differences mapped in the visible. These differences can be much more evident and/or diagnostic when observed...
at other wavelengths that should produce higher albedo contrasts corresponding to different mineralogic regimes. In particular, in the near-IR region, the degree of oxidation of basalts affects the slope from 0.5 to 0.8 microns, iron oxides (Fe$^{3+}$, Hematite, Goethite) have diagnostic bands between 0.5 and 1 micron, the "ferrous" band at 0.9-1.1 microns and around 1.5 microns can discriminate between various pyroxenes and olivines, and the 2-2.5 micron region can be used to differentiate between various clays, water of hydration, and similar OH-bearing materials.

The albedo contrasts can be (and for Mars, frequently are) masked by desert varnish, dust coating and atmospheric scattering, all of which tend to subdue or even mask underlying spectral features. These problems can be ameliorated by finding or creating fresh surfaces (requires high resolution or close proximity) and/or by having very good signal-to-noise to allow discrimination of absorptions having low contrast. The latter approach is also enhanced by utilizing high spatial resolution (to get limited mineralogic variation in a single field) and high illuminance.

Strontium titanate (SrTiO$_3$) is a popular host for investigations of vibronic spectra because of the importance of lattice vibrations in determining the interesting structural, electrical, and acoustical properties of the material. It has the cubic perovskite structure at room temperature with one molecule per unit cell and O$_h^1$ space-group symmetry. Around 110 K a second- or higher-order phase transition takes place and the symmetry becomes tetragonal. X-ray analysis implies that there are perhaps two other phase transitions at 65 and 35 K which further lower the symmetry. The lattice dynamics of strontium titanate have been studied experimentally and theoretically. The phase transition at 110 K has also been the subject of numerous and varied investigations and is currently attributed to the precipitation of the lowest transverse-optic "soft" phonon mode at the corner of the Brillouin zone. The 35-K phase transition is associated with the soft mode at the corner of the zone.

Previous studies of the optical properties of ions in SrTiO$_3$ have centered around Eu$^{3+}$ and Cr$^{3+}$, and some work has been done on a few other rare earth and transition-metal ions. From ionic-size considerations and electron-spin-resonance data it is generally presumed that the rare-earth ions substitute for Sr$^{2+}$ ions and the transition-metal ions go into Ti$^{4+}$ sites. Charge compensation has been found to take place non-locally. Both the strontium and titanium ions have O$_h$ site symmetry in the high-temperature phase of the lattice. The vibronic spectrum of europium-doped strontium titanate has been reported by Weber and Schaufele and that of chromium-doped strontium titanate has been reported by Stokowski and Schawlow and by Grabner. Although the Eu$^{3+}$ vibronics appear only as weak, unresolved structure on the side of the zero-phonon line, several peaks can be associated with specific phonon modes through the calculation of vibronic selection rules and comparison with other data. The Cr$^{3+}$ vibronic sideband exhibits much more pronounced structure. Although no detailed analysis has been made in this case, comparison with other data has led to the association of several vibronic peaks with specific phonon modes.

In this paper we report the results of a detailed investigation of the vibronic spectra of chromium-doped strontium titanate. An analysis of the low-energy (phonon emission) fluorescence vibronic sideband at low temperatures implies that the nature of the electronic part of the vibronic transition is predominantly forced electric dipole. Based on this result, vibronic selection rules were determined for phonons at various points in the Brillouin zone. Then by comparison with neutron scattering and infrared-absorption data, and by taking into account the vibronic selection rules, the peaks in the one-phonon contribution to the vibronic spectra were associated with transitions involving specific phonon modes. The high-energy (phonon-absorption) fluorescence vibronic sideband was investigated to better observe the low frequency phonons, especially the soft transverse optic modes. An effective density of phonon states was determined from the projected one-phonon vibronic sideband. This was used to obtain an estimate of the real phonon density of states and compared to that determined from fitting lattice-dynamics calculations to neutron scattering data.

The effective density of states obtained from the vibronic spectra was also used in fitting the temperature dependence of the widths and positions of the zero-phonon lines and the widths, positions, and intensities of an impurity-induced local mode.
The experimental procedure is described briefly in Sec. II, and the analysis of the vibronic sidebands is presented in Sec. III. The temperature dependence of the widths of the zero-phonon lines and the local mode is discussed in Sec. IV. Finally a short discussion of this research results is summarized in Sec. V followed by an example of the application of this electron-phonon interactions in Sec.VI.

II. EXPERIMENTAL

The SrTiO₃:Cr³⁺ crystal used in these experiments was obtained from the National Lead Co. and contained 0.02% Cr₂O₃ by weight. It was mounted on the cold finger of an Air Products Displex Helium refrigerator capable of varying the temperature from about 8 K to room temperature.

For measuring the fluorescence spectrum, the sample was illuminated with light from an AH-6 1000-W high-pressure mercury lamp filtered through 4 cm of saturated CuSO₄. The fluorescence emission was chopped and focused onto the entrance slit of a Spex 1-m scanning monochromator. The signal was detected by a cooled RCA C31034 photomultiplier tube, amplified by a PAR model 128 lock-in amplifier, and recorded on a strip-chart recorder.

Fluorescence decay times were made using a Xenon Corporation Model 457 Nanopulser with a pulse width of 10 nsec as an excitation source. The signal was built up using single photon counting and multichannel scaling techniques with a 256 channel multichannel analyzer.

Figure 3 shows the fluorescence spectrum of SrTiO₃:Cr³⁺ at about 8 and 150 K. At low temperatures the sharp zero-phonon lines (R₁ and R₂) are split by about 4.4 x 10⁻⁴ eV whereas in the high-temperature cubic phase only one R line appears. The low-energy vibronic sideband appears as a series of peaks spread over a range of about 0.15 eV from the R lines. The intense sharp peak at 1.491 eV in the low-temperature spectrum has been attributed by Stokowski and Schawlow to an impurity-induced local mode because it does not correspond to any known phonon frequency of strontium titanate and it does not appear in the vibronic sideband of Mn⁴⁺ in SrTiO₃. Since the normal-mode phonon frequencies in SrTiO₃ extend to about 0.1 eV from the R lines, the observed sharp peak in the spectrum is not a local mode in the strict definition. It lies on the high-energy side of a host phonon peak containing contributions from TO₂(Γ) and LO₂(Λ) modes among others. As shown in Fig. 1, it is more like a gap mode at low temperatures and a band resonant mode at high temperatures. However, for simplicity's sake we will continue to refer to it as a local mode. The first harmonic of the local mode appears at about twice the separation from the R lines as the fundamental. As the temperature increases, the R lines broaden, shift to higher energy, and decrease in intensity, and their splitting decreases. Similarly, the local mode broadens, decreases in intensity, and shifts to lower energy relative to the R lines. The rest of the vibronic sideband increases in intensity as the temperature increases, and the structure becomes less distinct.

Among the more interesting phonon modes in strontium titanate are the low-frequency transverse-optic modes, which lie within about 0.015 eV of the zero-phonon lines in the vibronic spectrum. Although some faint structure is observed in this region in the low-energy phonon emission sideband of Cr³⁺ shown in Fig. 1, it appears on the side of the broad, intense peak 0.015 eV below the R lines whose tail extends throughout this region. In an attempt to observe these low-frequency modes more distinctly, we also measured the vibronic sideband on the high-energy, or phonon absorption side of the R lines. At low temperatures, the high-energy vibronic transitions are less intense than the corresponding low-energy transitions due to the lack of phonons available for absorption, but the low-frequency phonon modes of interest here
are populated at rather modest temperatures. Figure 4 shows the high-energy vibronic spectrum at three different temperatures. More than 20 peaks can be observed in these spectra within 0.015eV of the zero-phonon lines, which represents more low-frequency structure in the phonon spectrum than has been seen by any other technique.

Figure 4. High-energy fluorescence vibronic sideband of SrTiO$_3$:Cr$^{3+}$ at about 8, 40, and 110 K.

It is interesting to observe that the intensities of most of the prominent peaks in the phonon absorption sideband do not increase with temperature proportionally to the phonon occupation numbers as expected. Instead, the intensities increase to a maximum at about 40 K and then decrease. A similar temperature dependence has been observed for the intensities of some of the low-frequency neutron scattering peaks. For soft modes this can be explained by the temperature dependence of the phonon frequency, which appears in the denominator of the expression for the transition rate. It would be interesting to observe the frequency shifts of the soft modes near the 110K phase transition. Unfortunately, by this temperature the R lines have broadened and the vibronics have decreased in intensity to such an extent that it is difficult to observe this effect.

The vibronic peaks and decay characteristics observed in both the high-energy and low-energy, or phonon absorption and emission, sidebands at low temperatures can be found in Reference 2.

III. VIBRONIC SIDEBANDS

The fluorescence spectrum of SrTiO$_3$:Cr$^{3+}$ appears to be an interesting mixture of magnetic dipole and phonon-forced electric dipole transitions. Burke and Pressley$^{13}$ have investigated the Zeeman spectra of SrTiO$_3$:Cr$^{3+}$ and concluded that the $R_1$ and $R_2$ zero-phonon lines arise from magnetic dipole transitions between the $^2E_g$ excited state and the $^4A_{1g}$ ground state, which are split by small amounts at low temperatures by the non-cubic distortions of the lattice. The same conclusion was reached by Stokowski and Schawlow$^{11}$ on the basis of studies of the polarization dependence of the intensity ratio of the $R_1$ and $R_2$ lines.

The vibronic sidebands, at least in the one-phonon energy range, appear to be largely electric dipole in origin. While electric dipole transitions between electronic states of the same parity are normally forbidden, they can become allowed if the electron-phonon interaction mixes in electronic states of opposite parity. For the 8K fluorescence spectrum shown in Fig. 1, the ratio of the integrated intensity of the zero-phonon lines to that of the vibronic sideband is roughly 0.39. If the sideband were all magnetic dipole in nature, this would correspond to a total Huang-Rhys factor of about 0.95. With a Huang-Rhys factor of this magnitude, two phonon emission processes would make substantial contributions to the total spectrum, and as we will see in more detail later, the near gap just above the local mode would not occur. As previously mentioned, the phonon density of states in pure SrTiO$_3$ extends up to an energy of approximately 0.1 eV.$^5$ The fluorescence spectrum of SrTiO$_3$:Cr$^{3+}$ extends up to an energy of approximately 0.1 eV.$^5$ The fluorescence spectrum of SrTiO$_3$:Cr$^{3+}$ appears to be dominated by one-phonon processes, and extends only into the two-phonon range. This is consistent with vibronic side-bands produced by phonon-forced electric dipole transitions.

However, magnetic dipole transitions may also contribute to the sidebands, particularly if their intensity is concentrated in narrow frequency regions.

The frequency dependence of the spectral intensity near the zero-phonon lines provides further evidence that the sidebands are primarily forced electric dipole in nature. Vredevoe$^{14}$ has studied the shape of the one-phonon spectrum in the limit of long phonon wavelengths for substitutional impurity ions in the rock-salt and zinc-blende structures. In the zinc-blende lattice,
he found that the sideband intensity should be proportional to \( \omega_0 - \omega_0^0 \) and to \( \omega_0^0 \) for forced electric dipole and magnetic dipole transitions, respectively, where \( \omega_0 - \omega_0^0 \) is the photon frequency relative to the zero-phonon line. In the rock-salt lattice, the intensity near the zero-phonon line varies as \( \omega^0 - \omega_0 \) and \( \omega^0 \) for electric dipole and magnetic dipole transitions, respectively.

The low-temperature phases of SrTiO3, like the zinc-blende lattice, do not have inversion symmetry. As indicated by the small splitting of the R lines at 8K and the insensitivity of the sideband structure to the phase transition at 110K, the low-temperature distortions away from O3 symmetry have an essentially negligible effect on the vibronic spectrum over most of its frequency range. However, the very low (relative) frequency behavior of the sideband will be determined by the non-cubic distortions at these frequencies, since this would give an \( \omega^0 \) dependence rather than some higher power law.

Vibronic sidebands arise, of course, from phonon-impurity electron interactions. The kind of interaction terms of interest for the SrTiO3:Cr3+ spectrum is well illustrated by the point-charge model, which is the model used by Vredevoe. The impurity lattice site is taken as the origin, and \( r \), is the electronic coordinate relative to the impurity ion core. \( R(l_i) \), \( u(l) \), and \( z(l) \) denote the equilibrium position, displacement from equilibrium, and effective charge, respectively, of the ion at the site \( l \). With the assumptions that \( |rl| \ll |R(l_i)| \) and \( |u(l) - u(0)| \ll |R(l_i)| \), the crystal potential energy of the impurity electron can be expanded in a Taylor series,

\[
\psi(r) = - \Xi'_i e^2 z(l)/|R(l)| - rl + \Xi'_i e^2 z(l)|R(l)|^3 \ast \\
\{R(l) \ast [u(l) - u(0)] \ast + \frac{1}{2} [u(l) - u(0)] \ast \\
D(R(l)) \ast [u(l) - u(0)] \ast - \Xi'_i e^2 z(l)|R(l)|^3 r \ast \\
D(R(l)) \ast [u(l) - u(0)] \ast + .... (1)
\]

Here \( \Xi'_i \) denotes the sum over sites \( l \neq 0 \), and \( D(X) \) is the dipole-dipole tensor,

\[
D_{ab}(x) = \delta_{ab} - 3 \chi_{ab} x^2 /|x|^2.
\]

The first term in Eq. (1) does not involve the ionic displacements; it affects only the static electronic energy levels, and cannot give rise to any vibronic structure in any optical transition. The second two terms are linear and quadratic in the ionic displacements, but do not involve the electronic coordinate. The matrix elements of these terms are therefore diagonal in the electronic states, and can by themselves produce vibronic sidebands only for allowed transitions, that is, for electric dipole transitions between electronic states of opposite parity or magnetic dipole transitions between electronic states of the same parity. The final term is bilinear in the electronic and phonon coordinates. For any electronic state, this term gives a dynamic admixture of states of opposite parity. Such an interaction allows electric dipole transitions between electronic states of the same parity, or magnetic dipole transitions between states of opposite parity. In the two-phonon and higher-order contributions to the total spectrum, interaction terms like the second and last in Eq. (1) can act in combination to yield structure which neither term could produce independently.

The full Hamiltonian for the impurity electron-phonon system can be written in the form

\[
H = \epsilon_0 + H_p + H_{ep},
\]

\[
H_0 = \Xi_m |\psi_m > - \Xi_m |\psi_m |
\]

\[
H_p = \Xi_\lambda \hbar \omega_\lambda (a_\lambda^+ a_\lambda + \frac{1}{2})
\]

\[
H_{ep} = \Xi_{m' m} |\psi_m > |\psi_{m'} > \{ (a_{m'} a_m^+ ) \} - |\psi_m |
\]

Here \( \psi_m > \) is an unperturbed electronic state, and \( a_\lambda (a_\lambda^+ ) \) is the destruction (creation) operator for the phonon mode \( \lambda \) of frequency \( \omega_\lambda \). In general, it is most convenient to diagonalize the phonon Hamiltonian in the initial electronic state of the optical transition of interest, in which case \( \lambda \) denotes the phonon modes for the impurity in its initial state. In the electron-phonon interaction Hamiltonian \( H_{ep} \), \( I_{mm'} \{ (a_m a_{m'}^+) \} \) is a phonon operator which may include not only linear but higher-order terms in \( a_m \) and \( a_{m'}^+ \). The second and third terms in Eq. (1), for example, make contributions to \( I_{mm'} \) which are diagonal in the electronic states \( (m = m') \) and first and second order, respectively, in the phonon creation and destruction operators. The last term
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in Eq. (1) mixes electronic states of opposite parity and is linear in a\textsubscript{i} and a\textsuperscript{*}\textsubscript{i}.

The symmetry of the phonon operators to I\textsubscript{mm}, can be determined from the transformation properties of the electronic states I\textsubscript{vm}, I\textsubscript{vm#}, and the point group of the defect. As previously noted, the non-cubic distortions of the SrTiO\textsubscript{3} lattice in its low-temperature phases appear to have very minor effects on the sidebands, so we will assume O\textsubscript{h} site symmetry for our discussion of phonon selection rules. The Hamiltonian must be invariant under the operations of the point group, that is, it must transform as the totally symmetric (A\textsubscript{1g}) representation of O\textsubscript{h}. If the electronic states I\textsubscript{vm}, I\textsubscript{vm#} transform according to the representations r(m) and r(m#), then the allowed symmetries of the phonon operator, I\textsubscript{mm}(a\textsubscript{i}, a\textsuperscript{*}\textsubscript{i}) are those representations contained in the direct product r(m) x r(m#). Through quadratic coupling terms, we have

\[ I_{mm} = \sum_{\gamma \nu} (\sum_{\lambda} V_{mm}(\lambda; \gamma\nu)(a\textsubscript{i} + a\textsuperscript{*}\textsubscript{i}) + 1/2\sum_{\lambda\delta} V_{mm}(\lambda; \gamma\nu) \]

where \( \gamma \) runs over the irreducible representation contained in \( \Gamma(m) \times \Gamma(m#) \) and \( p \) labels the members of the various irreducible representation basis sets. For simplicity, we have assumed that no irreducible representation \( \gamma \) occurs more than once in \( \Gamma(m) \times \Gamma(m#) \) and that the phonon creation and destruction operators appear in the combination a\textsubscript{i} + a\textsuperscript{*}\textsubscript{i}, but these simplifying assumptions can readily be lifted.

For allowed electric or magnetic dipole transitions, diagonal interactions I\textsubscript{vm} \rarrow I\textsubscript{vm}, I\textsubscript{mm} \rarrow I\textsubscript{mm}, in the final and initial states are generally responsible for the sidebands.\textsuperscript{18-21} For the SrTiO\textsubscript{3}:Cr\textsuperscript{3+} fluorescence spectrum, the initial- and final-state direct products are \( E_g x E_g = A_{1g} + A_{2g} \) and \( A_{2g} x A_{2g} = A_{1g} \). Thus only \( A_{1g}, A_{2g}, \) and \( E_g \) phonons or combinations of phonons may appear in any magnetic dipole contributions to the sidebands. The linear coupling terms in Eq. (8) for \( m = m' = A_{2g}, E_g \), can involve only \( A_{1g}, A_{2g}, \) or \( E_g \) phonons. In the quadratic coupling terms, however, while the product operators must transform as one of these even modes, the factors in the products may be both even or both odd. For example, \( T_{1u} x T_{1u} = A_{1g} + E_g + T_{2g} + T_{1g} \), so pairs of \( T_{1u} \) phonons give a quadratic coupling term of acceptable \( (A_{1g}, \) or \( E_g) \) symmetry.

The matrix elements for the phonon-forced electric dipole sidebands of the SrTiO\textsubscript{3}:Cr\textsuperscript{3+} lines involve products of the form \( I_{vm} \rarrow r < I_{vm}, I_{vm#} \) and \( I_{mm} \rarrow r < I_{mm}, I_{mm#} \), where \( f = A_{2g}, \) and \( i = E_g \) and \( I_{vm#} \) is an odd intermediate state. The electric dipole operator \( r \) transforms as \( T_{1u} \), so the allowed intermediate states must transform as \( T_{1u} \) or \( T_{2u} \) since \( A_{2g} x T_{1u} = T_{2u} \) and \( E_g x T_{1u} = T_{1u} + T_{2u} \). The phonon-coupling operators \( I_{mm} \) and \( I_{mm} \) must then transform according to \( T_{1u} \) or \( T_{2u} \). An equivalent but more direct demonstration of the same conclusion is provided by the triple direct product \( E_g x T_{1u} x A_{2g} = T_{1u} + T_{2u} \).

Figure 5. SrTiO\textsubscript{3} Unit Cell and Its First Brillouin Zone

The Brillouin zone (BZ) for SrTiO\textsubscript{3} is shown in Fig. 5 with points of high symmetry indicated. There are fifteen phonon modes at each point in the Brillouin zone. The transformation properties of the phonons along the principal symmetry directions have been determined by Cowley.\textsuperscript{4} We wish, however, to know the projections of the phonon modes at the various points in the BZ onto the irreducible representation of the point group of the defect, O\textsubscript{h}. If the O\textsubscript{h} projection of a phonon mode contains \( T_{1u} \) or \( T_{2u} \), then the phonon can contribute to the forced electric dipole sideband. If it does not contain one of these two modes, then electric dipole transitions involving such phonons are forbidden. Table II summarizes the vibronic selection rules obtained for transitions from an \( E_g \) state to other even electronic states. The majority of the phonon modes are allowed for \( E_g \rarrow A_{2g} \) transitions, but at the R, X, and M points, where the group of the wave vector has inversion symmetry, all of the even modes and some of the odd modes are forbidden.

Some of the peaks in the vibronic spectrum can now be tentatively identified with transitions involving specific phonon modes by comparing with other data and accounting for vibronic selection rules. Figure 6 shows the low-energy vibronic sideband at 8 K in comparison with
neutron scattering curves for five different directions in the Brillouin zone. The circles at the \( \Gamma \) point represent frequencies observed in infrared absorption.\textsuperscript{22-25} The circle with the cross in it at 0.1023 eV indicates a mode observed in both infrared absorption and neutron scattering.

The correlation between neutron scattering, infrared absorption, Raman scattering, and vibronic spectra data can be found elsewhere.\textsuperscript{2} First-order Raman scattering is allowed only in the low-temperature phase where the \( R \) point becomes the center of the Brillouin zone. Much of the detailed structure observed in the high-energy (phonon absorption) sideband cannot be identified with specific phonon modes. Some of this may be associated with the vibronics of the \( R_3 \) line. Other peaks may be attributed to the splitting of some of the phonon modes due to the tetragonal distortion which is difficult to resolve in the less structured low energy sideband. The phonon splittings in going from cubic to tetragonal (\( D_{4h}^8 \)) symmetry have been worked out only at the \( R \) point.\textsuperscript{7,8} A total of about 36 vibronic peaks can be associated with specific phonon modes.

While it is relatively easy to account for the sidebands in the one-phonon region, it is more difficult to determine the origin of the observed spectrum from the local mode out through its first harmonic. For the sake of brevity, we will refer to this portion of the spectrum as the local-mode sideband. In the perfect-crystal density of states, there is one isolated peak above the local mode at \( \hbar \omega/2\pi \sim 0.1 \text{ eV} \), which may give a one-phonon peak in the energy range of the local-mode sideband.

There may also be true local-mode peaks in this energy range, but their number must be limited to a few, if any, and their widths would necessarily be narrow since the concentration of \( \text{Cr}^{3+} \) impurities is very low. The bulk of the local-mode sideband must therefore arise from one or both of two sources: multi-phonon processes within the linear coupling approximation, or quadratic or higher coupling. In addition, the local mode, its harmonic, and the local-mode sideband may have their origins, separately or together, in forced electric dipole or allowed magnetic dipole transitions. Symmetry arguments provide a check on the internal consistency of any proposed explanation of the total spectrum.

A reasonably good fit to the total spectrum could be obtained with a simple combination of linear and quadratic coupling if the sidebands, like the zero-phonon lines, were all allowed magnetic dipole in nature. Although this seems clearly not to be the case, the analysis is still instructive. Diagonal electron-phonon interactions \( l_{nm} \) in the...
final and initial states are assumed to be most important. In the quadratic coupling terms, only those products which include the local mode as one or both of their factors are retained. The simplest additional simplifying assumption that can then be made is that the quadratic coupling coefficients involving the local mode are proportional to products of linear coupling coefficients,

$$W_{mn}(\lambda \lambda') = \alpha V_{mn}(\lambda) V_{mn}(\lambda') (\delta_{\lambda L} + \delta_{\lambda' L} - \delta_{\lambda L} \delta_{\lambda' L}),$$

(7)

where $L$ denotes the local mode, and the sum of Kronecker deltas in Eq. (9) is such that double counting is avoided for $\lambda = \lambda' = L$. From Eq. (8), the electron-phonon coupling operators $I_{mn}$ then have the form

$$I_{mn} = \sum_i V_{mn}(\lambda) (a_i + a_i^*) + \frac{1}{2} \alpha \sum_{\lambda \lambda'} V_{mn}(\lambda) *$$

$$V_{mn}(\lambda') (a_i + a_i^*) (a_i + a_i^*)$$

$$* (\delta_{\lambda L} + \delta_{\lambda' L} - \delta_{\lambda L} \delta_{\lambda' L}).$$

(8)

Equations (7) and (8) are written as if the local-mode peak had no width, but they are easily generalized to include the observed shape of the local-mode peak; this was done for the calculations discussed below.

With the interactions described by Eq. (8), the low-temperature fluorescence spectrum of SrTiO$_3$:Cr$^{3+}$ can be fitted by the iterative deconvolution techniques applied by one of the authors and co-workers to the optical spectra of the N$_1$ center in NaCl and the M(C$_2$H$_5$)$_2$ center in MgF$_2$. The results are shown in Fig. 7. The fit to the experimental data is essentially exact out through the local-mode peak because one-phonon processes are almost totally dominant in this frequency range; the Huang-Rhys factor for the one-phonon processes has the value $S = 0.3$ for the fit shown. Beyond this trivial agreement with experiment in the one-phonon energy range, the fit to the local-mode sideband and the first harmonic of the local mode is reasonably good in view of the extremely simple form assumed for the quadratic coupling coefficients.

The fit to experiment shown in Fig. 7 demonstrates several points. First, a one-phonon peak at $\hbar \omega/2\pi \sim 0.1eV$ is probably responsible for the corresponding peak in the fluorescence spectrum above the local mode. Second, the convolution of the one-phonon spectrum with itself generates a rather featureless two-phonon band, as shown in Fig. 5(b). The magnitude of the two-phonon spectrum in Fig. 5(b) is small because of the low Huang-Rhys factor for the fit, but a larger Huang-Rhys factor would simply scale up the two-phonon spectrum by a factor of $1/2S^2$ without introducing any further structure in it. In particular, if the Huang-Rhys factor had the value $S = 0.95$ needed to reproduce the observed zero-phonon: total integrated intensity ratio $e^{-S} = 0.39$, the two-phonon spectrum would rise to a maximum value of about 0.25 just above the local mode, which is several times larger than the observed spectral intensity in this region. Third, the local-mode sideband and the local-mode harmonic appear to at least qualitatively replicate many of the features of the one-phonon spectrum out through the local mode.

Figure 7. (a) Fit between the observed (solid line) and the calculated (dotted line) vibronic sidebands which was obtained from the simple model described by Eq. (8) with $\alpha = 350eV^{-1}$ and $S = 0.3$. (b) One (dash-dot line), two (dash-double-dot line), and three(dash-triple-dot line), phonon contributions to the calculated total sideband (dotted line). (c) Calculated one-phonon sideband (solid line) and the contribution due to quadratic coupling between the local mode and the lattice modes (dash-dot line).
ELECTRON-PHONON INTERACTION ON OPTICAL SPECTRA OF NANOELECTRONIC DEVICES - Q. Kim

While the fit to the observed fluorescence spectrum shown in Fig. 7 is reasonably good, it appears to be unrealistic because of the evidence for the importance of forced electric dipole transitions. However, it should be emphasized again that magnetic dipole transitions may make non-negligible contributions to the one-phonon spectrum, and furthermore, that they may dominate in all or part of the two-phonon range. For example, the quadratic coupling explanation just described for the local-mode sideband and the local-mode harmonic may apply even if the entire one-phonon spectrum is produced by forced electric dipole transitions involving odd (T1, T2) phonons. The quadratic coupling of the odd mode with other odd phonons would then yield an even phonon operator which could be involved in allowed magnetic dipole transitions.

The one-phonon vibronic sideband can be used to obtain information on the phonon density of states of the host crystal. However, what is observed directly is an effective density of states, which is the real density of states modified by vibronic selection rules, by the frequency dependence of the electron-phonon coupling parameters, and by the distortions caused by the impurity ions in the lattice. In order to determine the frequency dependence of the electron-phonon coupling parameters, a detailed model must be developed for the lattice dynamics in the presence of the impurity. Such approaches have been carried out for several simple systems, but a detailed theoretical treatment of the electron-phonon coupling for the SrTiO3:Cr3+ system is beyond the scope of this paper. Instead, we will show only that there is substantial correlation between the observed structure in the one-phonon vibronic sideband and the results of the shell-model calculations of the perfect-crystal density of states.

In the long-wavelength limit, the relation between the effective density of states g(ω) for vibronic transitions and the phonon density of states ρ(ω) in the host lattice is ρ(ω) = ωg(ω). Figure 8 shows a comparison between ωg(ω) obtained from the one-phonon spectrum in Fig. 7, omitting the local-mode peak, and the perfect-crystal density of states calculated by Stirling. The peak positions in the two curves are in generally good agreement. The peak at 0.09eV in the shell-model results arises from the highest-frequency optic modes. As Stirling notes, the calculated frequencies for these modes are very model dependent, and the particular shell model used for the curve in Fig. 8 (Stirling's model 5) yields a value for the highest q = 0 optic-mode frequency which is roughly 10% low; the peak should fall at about 0.1eV as it does in the vibronic density of states. The perfect-crystal peak at 0.0154eV arises from contributions from phonons around several points in the Brillouin zone. Some of these are forbidden by the selection rules for electric dipole transitions, which may account for the relatively low intensity of this peak in the vibronic density of states.

IV. TEMPERATURE DEPENDENCE OF WIDTHS OF ZERO-PHONON LINES

The line widths Γ(R1), and Γ(R2) of the zero-phonon lines can be attributed to contributions from several different processes,

\[ \Gamma(R_i) = \Delta E_o + \alpha(R_i) \int d\omega \omega \rho'(\omega)^2 n(\omega) x[n(\omega) + 1] \]

The first term, \( \Delta E_o \), is temperature independent and is due to varying microscopic strains in the crystal. The second term arises from quadratic coupling, and represents the continual emission and absorption of virtual phonons (i.e., the Raman scattering of phonons) by the.
impurity ion. In the integrand of this term, \( \rho'(\omega) \) is an effective density of states for these processes, and \( n(\omega) = 1/(e^{\omega/kT} - 1) \) is the thermal occupation number for a phonon of frequency \( \omega \). The last two terms are lifetime broadening contributions due to direct electronic transitions between the slightly split components of the initial electronic multiplet in which a real phonon is absorbed or emitted; \( \omega_{12} \) is the (temperature-dependent) \( R_1-R_2 \) difference frequency. The coupling parameters \( \alpha(R_i) \) and \( \beta(R_j) \) are treated as disposable parameters.

We have attempted to fit our data using three different models for the effective density of states \( \rho'(\omega) \) in Eq. (11): a Debye distribution, the vibronic density of states \( g_\nu(\omega) \) shown as the solid curve in Fig. 6, and an Einstein distribution. The latter represents coupling to only one phonon mode, for this case one of the soft-phonon modes. This model was included because Luders and Rankin\(^{29}\) found that the temperature dependence of the zero-phonon line width for europium doped strontium titanate could be explained by coupling to the soft mode.

V. DISCUSSION AND SUMMARY OF RESULTS

Through the use of vibronic selection rules, a number of vibronic peaks were tentatively associated with transitions involving specific phonon modes. Some of the unidentified peaks (especially the low-frequency peaks in the high-energy vibronic sideband) might be associated with phonon modes split by the tetragonal distortion. It would be useful if the symmetry properties of the phonons in the low-temperature phase would be determined.

An area where more work is needed is in developing better theoretical models for predicting the vibronic spectra. From such models, more accurate expressions for the phonon density of states and the host material element could be obtained.

The most interesting result obtained from analyzing the temperature dependence of the widths of the zero-phonon lines and the local mode was that the former was affected mainly by low-frequency phonons whereas the latter involved phonons of all frequencies. Similar analyses were made of the temperature dependence of the positions of the \( R \) lines and the local mode. Although phonon processes can be made to fit the data, there is some question as to the meaningfulness of the interpretation since it has been shown previously that the temperature dependence of the tetragonal distortion makes an important contribution to the shifts of the \( R \) lines at low temperatures\(^{30,31}\). The quadratic coupling should also affect the temperature dependence of the intensity of the local mode. The local mode can be considered as a zero-phonon line and the quadratic coupling region as a one-phonon sideband to this line. As the temperature is raised, more of the emission occurs in the sideband and less in the zero-phonon line. The experimentally measured temperature dependence of the intensity of the local mode has been reported elsewhere\(^{32}\) and fit theoretically using an expression involving a Debye distribution of phonons and a Huang-Rhys factor of 2.9. If the quadratic coupling region of the spectrum can actually be considered as a "sideband" of the local mode, then the Huang-Rhys factor should be given by the ratio of the integrated intensity of the quadratic coupling region to that of the local mode. This is found to give \( S = 2.11 \), which is consistent with the value found from fitting the temperature dependence of the local-mode intensity.

VI. NON-CONTACT MICROCHANNEL TEMPERATURE ASSESSMENT

Based on the effects on electron-phonon interaction on the optical emission infrared spectrum discussed above, a hot spot channel temperature of a 500nm GaAs metal semiconductor field effect transistors (MESFET) gate was experimentally determined by a non-contact technique during operation.

A test system was constructed utilizing the general setup and some of the equipment used in the Microelectronic Advanced Laser Scanner (MEALS).\(^{33}\) Utilizing the micromanipulator stage, a HeNe laser beam (\( \lambda = 632.8 \)nm) with a beam width of 0.4 microns was precisely adjusted to the exact gate position (resolution less than 100nm) of the GaAs MESFET device. Discriminating emission light from the illuminating light was achieved by placing a low-band pass filter between the reflecting mirror and the spectrometer, as shown in Figure 9. A lock-in amplifier, equipped with a cooled Hamamatsu R943-02 photomultiplier tube, was
used for the detection of standard synchronous signals. Data collection and manipulation was performed using a personal computer with the appropriate software tools.

A commercially available GaAs MESFET, with gate dimensions of 500nm, was mounted in the test fixture and emission spectra were successfully obtained. The emission spectrum obtained by the test setup, indicates that this technique can be effectively manipulated to collect extremely faint gate emission spectra. The collected emission spectrum, as shown in Figure 10, from the free excitons and impurity bound excitons were identified and measured at two different temperatures. The band shift of the free-exciton emission of the un-powered GaAs MESFET gate was calibrated by the two different temperatures of 299.0 and 84.7 K. The shift was 10.0 nm. In order to remotely measure the local temperature rise of the miniature 500nm-size gate due to the device operation, the emission band shift of the same gate from un-powered to powered were monitored at one (84.7 K) of the calibrated temperatures. The shift was 4.5 nm.

As was discussed above, the emission bandwidth of a semiconductor material is inversely proportional to the material temperature due to the first approximation of the electron-exciton interaction at this temperature range. Thus utilizing the impurity band-shifts, one can calculate the localized hot gate temperature rise of the powered device under test utilizing the impurity band positions measured by a conventional spectrometer. Using Equation (10) and information summarized in Table I, one can show that the localized hot gate temperature of the device was risen by 75 K during the operation at 84.7 K. The temperature rise was also compared with conventional state-of-the-art infrared spectrum measurement technique, of which resolution is between 15 and 100 microns. The average temperatures rise was about 15-45 K.

Table I. Summary of band shift data

<table>
<thead>
<tr>
<th>Test Temperature (K)</th>
<th>Wavelength (nm)</th>
<th>Power Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>299</td>
<td>877</td>
<td>No</td>
</tr>
<tr>
<td>84.7</td>
<td>871.5</td>
<td>Yes</td>
</tr>
<tr>
<td>84.7</td>
<td>867</td>
<td>No</td>
</tr>
</tbody>
</table>

Gate Temperature Rise = T - T_o
= (299.0 K - 84.7 K) x (871.5 - 867.0)/(877.0 - 867.0) = 75 K.
Lifetime estimation of power devices in space application, such as GaAs MESFETs, depends closely upon the operating temperature of the several nm-size power MESFET channel. Currently, the only commercially available non-contact techniques to characterize the thermal distribution of the powered device is passive infrared sensing. However, this method does not inform the true local gate information of temperature with resolution being limited to 15 microns, which is inadequate for state-of-the-art devices with gate structures less than one micron.

This new non-destructive 500nm-size spot temperature assessment technique was reported, for the first time. A non-destructive a micron-size spot laser beam provided by a laser excites an extremely small local area of the gate channel of a GaAs MESFET under various operating conditions. The data collected shows a much higher localized “hot spot” temperature of the device than observed using typical IR techniques. This is due to the high resolution capabilities of this technique. Given the state of the experimental test system, we estimate a spatial resolution of about 500nm and a spectral resolution of about 0.1 Angstroms. This provides 30 - 200 times finer spatial resolution than can be obtained using the best passive infrared systems available. The temperature resolution (< 0.01 K/μm) of this technique is depend upon the spectrometer used), and that it can be improved further.

The information obtained from this technique can be used to estimate device lifetimes for critical applications in long-term space missions and for measurement of channel temperature of devices under actual operating conditions. Another potential use of the novel technique can be as a cost-effective prescreening tool for determining the “hot spot” channel temperature of devices under normal operating conditions which can further improve device design, yield enhancement, and reliable operation.

ACKNOWLEDGMENT

The research described in this paper was carried out both at Oklahoma State University and at Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not constitute or imply endorsement by the United States Government or the Jet Propulsion Laboratory, California Institute of Technology.

REFERENCES

15. Dynamic Jahn-Teller coupling –curs when the initial or final electronic state is a member of a multiplet of degenerate or nearly degenerate levels which are mixed by the electron-phonon interaction in such a way that the electron Hamiltonian within the multiplet cannot be diagonalized by a transformation which is independent of the phonon amplitudes (Refs. 14 and 15). In the cumulant expansion formalism of McCumber (Ref. 16), the lowest-order effects of dynamic Jahn-Teller coupling appear as two-phonon contributions to the spectrum, and as
corrections to the spectral moments. Although the initial multiplet ($^2E_g$) of the SrTiO$_3$:Cr$^{3+}$ fluorescence spectrum can be mixed by dynamic Jahn-Teller interactions with $E_g$ phonon modes, we will neglect this effect because of the evidence that the sidebands are predominantly forced electric dipole in nature, which requires coupling to odd or ungerade phonons.