I_1 Emission Line in CdS as a Phonon Spectrometer

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We demonstrate the use of the I_1 luminescence feature in the near-bandgap luminescence spectrum of CdS as a high-resolution phonon spectrometer by measurement of the phonon distribution resulting from a photoexcited heat pulse generated in a gold film evaporated on the crystal.

Analysis of the shapes of the luminescence spectra due to impurity levels in solids provides a means for deducing considerable information about interactions of phonons with electrons and impurity levels in the crystal. For systems in which these interactions are well understood, the luminescence spectra can be used to determine presence and *spectral distribution* of nonequilibrium phonons. One such system is the I_1 luminescence feature[1] of the semiconductor CdS. In this Letter we show that an analysis of the I_1 line shape allows one to determine the distribution of nonequilibrium acoustic phonons as a function of phonon energy. While phonon distributions can also be inferred from measurements of selective phonon absorption by stress-split donor levels in Ge[2] and by magnetic-field-split spin levels in various paramagnetic systems,[3] the unique properties of the I_1 emission line allow one to obtain the phonon distribution function simply and directly. We demonstrate this by presenting the experimentally determined distribution function for phonons generated by photoexcitation of a gold film evaporated on a CdS crystal.

A representative I_1 luminescence spectrum at 1.8°K is shown in Fig. 1(a). This relatively sharp luminescence feature, first studied by Thomas and Hopfield,[1] originates in the recombination of an exciton bound to a neutral acceptor impurity; Henry, Nassau, and Shiever[4] have shown that the responsible acceptors are Na or Li impurities. The I_1 feature can be decomposed into three components, (i) a no-phonon, sharp, central peak due to the recombination of the bound exciton, (ii) a broad, low-energy wing ("Stokes" side) due to the recombination with simultaneous *emission* of acoustic phonons, and (iii) and an anti-Stokes wing, absent at 1.8°K, due to recombination with simultaneous *absorption* of acoustic phonons. Hopfield[5] has analyzed these processes within the framework of a theory that neglects multiphonon interactions, but includes single-phonon interactions to all orders. His calculations are in excellent agreement with the experimental line shape and show that at helium temperatures, where only the first-order interactions are significant, the intensity of Stokes and anti-Stokes wings at energy $\mp E$ with respect to the central peak is proportional to $[1+\bar{n}(E)]M(E)$ and $\bar{n}(E)M(E)$, respectively. Here $\bar{n}(E)$ is the occupation number of phonons with energy E and the factor $M(E)$ depends on the strength of coupling between the bound excitons and the phonons. In equilibrium $\bar{n}(E)$ is given by $[\exp(E/kT)-1]^{-1}$. By taking the ratio of anti-Stokes to Stokes signal the matrix element factor $M(E)$ can be eliminated and the oc-

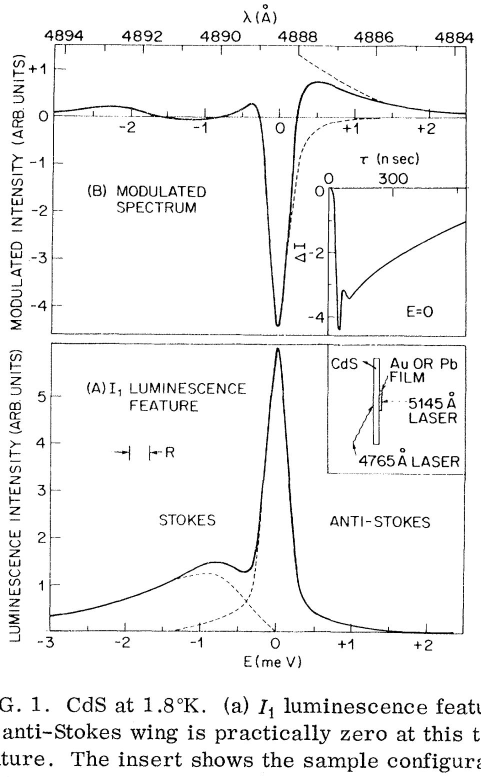

FIG. 1. CdS at 1.8°K. (a) I_1 luminescence feature. The anti-Stokes wing is practically zero at this temperature. The insert shows the sample configuration. (b) The modulated spectrum at 30-nsec delay. The insert shows a time-of-flight measurement. The spectrometer resolution is 0.25 meV. $E=0$ corresponds to 4888.5 Å.

cupation number $\bar{n}(E)$ at every E can be determined directly. We thus have a phonon spectrometer with energy resolution determined by the linewidth of the central peak, which can be as narrow as 0.05 meV,[1] and a response time of approximately 1 nsec corresponding to the I_1 lifetime.[6] We have tested this phonon spectrometer by determining the spectral distribution function of the phonons generated by photoexcited gold.

The sample configuration is shown in the inset of Fig. 1(a). The sample was a 40-μm-thick single-crystal platelet[7] of CdS, having two large (~ 5 mm × 2 mm) faces parallel to the crystal c axis. A 3000-Å-thick gold film was evaporated on one face. Two cavity-dumped Ar$^+$ lasers, producing ~15-nsec-wide pulses at a 10-kHz repetition rate, were used for these experiments. The first laser, at 5145 Å, was chopped by a mechanical chopper at ~400 Hz and was focused (~ 200 μm diam) on the gold film. The second laser, at 4765 Å,[8] was focused (~100 μm × 1 mm) on the opposite face of the crystal to excite the I_1 luminescence. The crystal was immersed in superfluid He at 1.8°K. Photoexcitation of the gold film resulted in the modulation of the intensity of the I_1 luminescence, which was measured directly with a lock-in amplifier. A continuously variable delay τ was introduced between the two lasers to obtain time-resolved measurements. Thus a two-pen recorder simultaneously recorded the modulated signal (i.e., the output of the lock-in amplifier) and the direct signal as a function of wave length or the delay time. Since the modulated signal was small (typically < 1%) the direct signal was a measure of the luminescence in the absence of the 5145-Å laser.

Photoexcitation of the gold film is expected to raise its temperature above the ambient by an amount proportional to the fourth root of the absorbed power. The phonons generated in the gold film propagate ballistically along the a axis of CdS ($\approx$ 40 μm thick) and arrive at the opposite face after delays of approximately 10, 22, and 23 nsec for the longitudinal, fast transverse, and the slow transverse modes, respectively. Since the pulsewidth is $\approx$15 nsec, the signals due to different modes merge into each other and give rise to a single peak for the ballistic phonons. Multiple reflections at boundaries and other scattering machanisms would give rise to a long tail following the arrival of ballistic phonons. An experimental plot of the modulated signal versus the time delay, shown in the inset of Fig. 1(b), is in agreement with these ideas and leads to the conclusion that the modulated signal at 30 nsec is due to the arrival of the ballistic phonons and *not* due to heating of CdS.

The spectrum of modulated intensity at $\tau = 30$ nsec is shown in Fig. 1(b). The signal at the I_1 peak is negative because the excess phonon density increases phonon-assisted recombination and reduces the intensity in the no-phonon peak. The signal is relatively large because the change in intensity at the peak is proportional to the *total* number of excess phonons. The signal in the anti-Stokes wing is positive because of the increase in these phonon-assisted transitions with increase in phonon density. The signal is smaller than at $E = 0$, because only phonons of energy E contribute to the modulated signal at energy $\pm E$. This simplified model for the changes produced by the excess phonons in the I_1 luminescence spectrum leads one to expect that the modulation signal be symmetrical about $E = 0$. The lack of symmetry in the experimental data shown in Fig. 1(b) indicates the presence of some complicating factors on the Stokes side. One possibility is a small shift in the energy of the I_1 peak.[9] This would produce appreciable changes on the Stokes side, but would leave the anti-Stokes side approximately the same. Since the modulated anti-Stokes intensity is proportional to the pho-

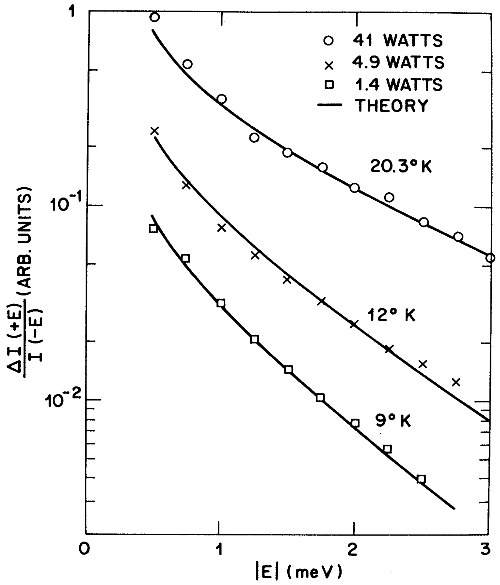

FIG. 2. The ratio of modulated anti-Stokes intensity to unmodulated Stokes intensity as a function of phonon energy E. The points are experimental, the solid curves are calculated from $\bar{n} = 1/[\exp(E/kT) - 1]$ for the temperatures indicated on the curves. The curves are arbitrarily displaced with respect to each other.

non density we only need to use this feature to determine the occupation number $\bar{n}(E)$ by taking the ratio of the *modulated* anti-Stokes signal [Fig. 1(b)] to the *unmodulated* Stokes signal [Fig. 1(a)]. In taking this ratio, we have obtained the unmodulated Stokes signal at small E by assuming that the central peak is symmetric. The modulated anti-Stokes signal is corrected by assuming that the line shapes of the central peaks are the same in the modulated and the unmodulated spectra. The dashed curves in Fig. 1 are drawn according to this procedure.

A plot of this ratio $\Delta I(+E)/I(-E)=\bar{n}(E)$ versus E is shown in Fig. 2 for three different excitation levels.[10] The figure also shows solid curves calculated from $\bar{n}(E)=1/[\exp(E/kT)-1]$ for three different temperatures. We see that the agreement between the calculated curves and the experimental points is excellent, and conclude that the phonon distribution generated by photoexcitation of the gold film can be well described by a temperature. The temperature determined in this way is proportional to the fourth root of the incident power as expected for the temperature variation of the Au film. These observations demonstrate that the I_1 luminescence feature can be used as a phonon spectrometer.

The I_1 phonon spectrometer is ideally suited for measuring nonequilibrium phonon distributions. Examples include the phonon fluorescence spectra of superconductors and their variation with external perturbations such as magnetic fields. It should also be possible to study quantitatively the transmission of phonons at interfaces and the effect of selective absorption or scattering of phonons by impurities in CdS. The I_1 phonon spectrometer thus opens up a wide range of possibilities, some of which we are currently exploring.

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[7] Strong, sharp, I_1 emission lines can also be observed on cleaved faces of many bulk crystals or bulk crystals which are doped with Na or Li [B. Tell, J. Appl. Phys. 42, 2919 (1971)].

[8] 4765-Å radiation is strongly absorbed by CdS whereas 5145 Å is not absorbed and does not affect the I_1 luminescence in any way.

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[10] The presence of I_2 luminescence $E=+11$ meV limits the range of measurement to about 4 meV. Removal of the impurities responsible for this feature would extend the range of the I_1 spectrometer to ≈ 12 meV, the cutoff energy for acoustic phonons in CdS.

Temperature- and Composition-Dependent Valence Mixing of Sm in Cation- and Anion-Substituted SmS Observed by X-ray Photoemission Spectroscopy*

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We have determined the interconfiguration mixing ratios (Sm^{+3}/Sm^{+2}) of 1.4 and 4.1 for $Sm_{0.81}Y_{0.19}S$ and $SmAs_{0.18}S_{0.82}$ at 295 K from their x-ray photoemission spectra. These ratios are observed to decrease reversibly by a factor of 2 at 110 K. The agreement of these results with valences deduced from lattice-constant measurements is direct evidence that configuration mixing is responsible for the anomalous temperature- and composition-dependence of the lattice constant.

A mixture of two configurations within the ground-state eigenstate of SmS and its solid solutions has recently been correlated with many unique and unusual properties, including (1) the dramatic pressure-induced semiconducting-to-metal phase transformation in SmS[1] which is a