Two-Phonon Indirect Transitions and Lattice Scattering in Si

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The probability of indirect transitions with the emission of two phonons has been calculated. Several of the intensity maxima in the intrinsic low-temperature emission spectrum of Si are explainable in terms of these transitions. Scattering matrix elements obtained from an analysis of the observed emission spectrum indicate that intervalley scattering is the dominant scattering mechanism for electrons in Si, with 0.023-ev and 0.046-ev longitudinal acoustic mode phonons umklapp scattering electrons between valleys on the same and on different crystal axes, respectively. The valleys are approximately 82% of the way from the center to the edge of the Brillouin zone. Optical mode scattering in the valence band is largely responsible for the anomalous temperature dependence of the intrinsic hole mobility.

HAYNES, Lax, and Flood[1] have observed peaks in the low-temperature recombination radiation spectrum of Si. They originally believed that these peaks corresponded to indirect transitions involving single phonons, two of which had rather high energies, 0.083 ev and 0.119 ev. The maximum phonon energy in Si, however, has been shown to be 0.064 ev by Brockhouse,[2] who suggested that processes involving two phonons might account for the two energetic "phonons" observed by Haynes et al. We have investigated theoretically the two-phonon indirect optical transitions which might be of greatest importance in a substance such as Si and have concluded that the experimentally observed intensities are in excellent agreement with predictions based on the two-phonon model. In addition, the exact intensity and position of the emission peaks give valuable information concerning the scattering of holes and electrons by optical mode and intervalley mode phonons.

For photon emission, the significant third order processes resemble the usual indirect optical recombination process[3] with an additional virtual scattering by phonon emission either initially in the conduction band or finally in the valence band. A second virtual intermediate state is involved for these processes, again either in the conduction band or in the valence band.

In order to facilitate comparison with experimental data, and in order to eliminate matrix elements and energy denominators common to the two processes, we have calculated the ratio R of integrated intensity for a two-phonon process to the integrated intensity for the corresponding single phonon process. R is given by

$$R=\frac{\pi}{2}\frac{\hbar\omega}{\hbar\omega+k\theta_i}\frac{|H_{ii}|^2 g_i}{(k\theta_i)^{\frac{1}{2}}}\left(1+\tfrac{3}{4}\frac{T}{\theta_i}\right), \qquad (1)$$

for $T\ll\theta_i$. $\hbar\omega$ is the mean energy of the photon emitted in the two-phonon process, H_{ii} is the matrix element for the optical mode or intervalley mode scattering in the ith band by spontaneous phonon emission, $k\theta_i$ is the phonon energy and $g_i E_i^{\frac{1}{2}}$ is the density of states in energy for scattering by these modes.

The main emission peak in Si is believed to be due to single phonon indirect transitions involving optical mode phonons of 0.058-ev energy. One would expect two-phonon transitions to use this same phonon plus another emitted while scattering between valence or conduction band states, and therefore the two-phonon emission peaks would be energetically below the single-phonon peak by just the energy of the additional phonon. In recent data of Haynes[4] on Si at 17.8°K there are two clearly resolved intensity maxima approximately 0.023 ev and 0.063 ev below the main emission peak. At this temperature another maximum can just be resolved 0.046 ev below the main peak.

Assuming the correctness of the two-phonon model, phonons of 0.023-ev and 0.046-ev energy could only correspond in Si to intervalley scattering processes. If we use Eq. (1) to obtain the product involving the matrix element H_{ii} and the density of states factor g_i from the experimental known ratio R, and then calculate the scattering of electrons using this information, we find that at 300°K intervalley processes involving 0.023-ev and 0.046-ev phonons contribute 56% and 22%, respectively, to the total scattering of electrons.[5,6] According to the calculations of Herring and Vogt[7] at least 20% of the scattering at 300°K will consist of intravalley scattering by the acoustic modes, so that essentially all of the remaining electron scattering seems to be accounted for by the intervalley processes. This consistency reflects on the correctness of the two-phonon model.

Data on the lattice vibrational spectrum of Si[2] indicates that a 0.023-ev phonon energy would correspond to umklapp scattering between valleys on the same axes by a longitudinal acoustic modes with wave-

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number 36% of the maximum wavenumber in the (1,0,0) direction. This places the conduction minima at 82% of the way from the center to the edge of the Brillouin zone. The 0.046-ev phonon corresponds to umklapp scattering between valleys on different axes using a phonon with wave number q given by $(1,0.18,0.18)2\pi/a$. Since the longitudinal acoustic and optical modes are degenerate at $q=(1,0,0)2\pi/a$ and, according to Brockhouse,[2] have phonon energies of 0.049 ev, the 0.046-ev intervalley phonon is probably a longitudinal acoustic mode.

The intensity maximum 0.063 ev below the main intensity maximum in Si corresponds in energy to a two-phonon process in which, in addition to the 0.058-ev phonon, an optical mode phonon is emitted during virtual scattering in the valence band. Although the virtual scattering may occur in a conduction valley, it seems unlikely that optical mode scattering in the conduction band is very significant. If we calculate the matrix element for optical mode scattering in the valence band from the experimental ratio R for the 0.063-ev intensity maximum, this matrix element squared is approximately 76% that which is required to explain the anomalous temperature dependence of the hole mobility in Si[5,6] on the basis of mixed acoustic and optical mode scattering with parabolic valence bands. Because of the small spin orbit splitting between the valence bands in Si it seems likely that the nonparabolic nature of these bands[8] would also contribute to the deviation of the temperature dependence of the hole mobility from a $T^{-\frac{3}{2}}$ law.

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Cross Relaxation Studies in Diamond*

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A microwave double resonance experiment performed on the paramagnetic nitrogen centers in diamond shows that in this system cross relaxation occurs via a four spin flip mechanism which exactly conserves Zeeman energy. In this process, which was first postulated by Bloembergen and co-workers in their paper on cross relaxation, two spins of the center line make a downward transition while a spin belonging to each satellite makes an upward transition. Simple rate considerations for this process indicate that if a saturating microwave field is suddenly applied to one of the three lines of the nitrogen spectrum, a weak probing microwave signal at either of the two other lines should register a definite change in absorption in a time T_{21}. Specifically, if T_{21} is much less than other relaxation times of the system, then setting the pump upon the center line should force the absorption at either satellite to drop to zero. Setting the pump at the position of one of the satellites, on the other hand, should reduce the center line absorption to $\frac{5}{8}$ its thermal equilibrium value but should increase the absorption measured at the other satellite by the factor 6/5. This behavior was precisely observed at 1.6°K, using a bi-modal cavity.

By resolving the rate at which a satellite decays to zero when the pump is set on the center line, T_{21} is measured for all five satellites in the three principal orientations: $H_0\|[100]$, $H_0\|[110]$, and $H_0\|[111]$. The measured anisotropy is discussed.

It is shown that the four spin flip transition may be used in special cases to establish continuous wave maser operation by inverting the population of one of the satellite lines. Steady state inversion of one of the nitrogen satellites is incidentally observed in a number of diamonds.

1. INTRODUCTION

RECENTLY Bloembergen and co-workers[1] have analyzed the processes of energy transfer between adjacent resonances in both nuclear and electronic spin systems. These authors consider that multiple spin reversals of neighboring spins which are induced by the dipolar and exchange interactions between the ions are primarily responsible for the transfer of energy between resonances. For a given multiple spin flip process to be important in the establishment of spin-spin equilibrium a necessary requirement is that the total Zeeman energy be nearly or exactly conserved by the process. This led Bloembergen et al. to suggest that in certain instances a relatively high-order process which conserves Zeeman energy may be more probable than a simple flip-flop between two spins whose resonance frequencies are sufficiently different that there is no appreciable overlap between the lines.

It occurred to us that the paramagnetic resonance of nitrogen centers in diamond[2] could be used to verify quantitatively the occurrence of a higher order spin flip process, the reason being that the characteristic resonance spectrum of three narrow, equally spaced hyperfine lines is compatible with only one multiple spin reversal process which exactly conserves Zeeman energy. This process (Fig. 1) consists of simultaneous double flip-flops and was invoked by Bloembergen and coworkers to explain qualitatively the cross saturation

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