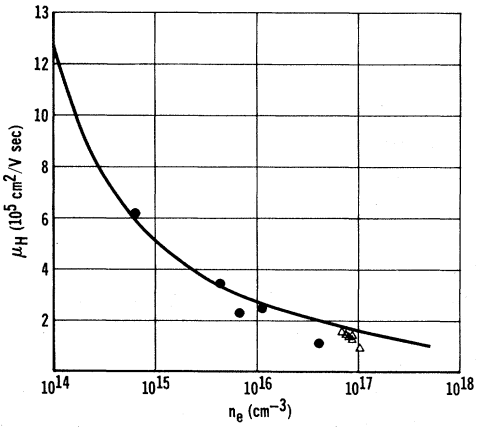

FIG. 1. Hall mobility of degenerate α-Sn as a function of electron concentration. Experimental points are from Ref. 4 (dots) and Ref. 5 (triangles).

mobility calculated using the values of E_g, Δ, and μ found by Groves et al.,[8] with an ϵ_0 of 24.[9] The results of this calculation are shown in Fig. 1 along with the experimental values.[4,5] The agreement is quite good over the whole range of concentrations and thus the anomalous low-concentration mobility does not appear to provide evidence for a strong concentration dependence in $\epsilon(q)$. In this calculation the anomalously high mobility at low concentration is provided by a combination of the reduction in large-angle scattering due to the almost pure p-like character of the wave function near the zone center and the decrease of effective mass with decreasing k_F. At the lowest concentration experimental point, the Fermi energy is only 0.001 eV and a crude estimate using Liu and Tosatti's[3] results indicates that the calculated mobility should be enhanced by a factor of ≈ 4 over the value shown here if the interband polarization effect is included. A more accurate calculation of this is in progress, although it is not expected that the estimate will be much changed.

The strong dependence of the dielectric constant of α-Sn on impurity concentration is a theoretical consequence, by way of the RPA, of the fact that the conduction-valence band degeneracy is symmetry induced. This peculiarity of the band structure is well established and, indeed, is the basis for the treatment of the differential cross section in this paper. Thus, these results strongly suggest that the RPA, as the principal physical approximation of the dielectric function calculation, considerably overestimates the interband polarization.

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[1]L. Liu and D. Brust, Phys. Rev. Letters 20, 651 (1968), and Phys. Rev. 173, 777 (1968).

[2]D. Sherington and W. Kohn, Rev. Mod. Phys. 40, 767 (1968).

[3]L. Liu and E. Tosatti, Phys. Rev. Letters 23, 772 (1969).

[4]E. D. Hinkley and A. W. Ewald, Phys. Rev. 134, A1260 (1964).

[5]O. N. Tufte and A. W. Ewald, Phys. Rev. 122, 1413 (1961).

[6]J. G. Broerman, Phys. Rev. 183, 754 (1969).

[7]E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[8]S. H. Groves, C. R. Pidgeon, R. J. Wagner, and A. W. Ewald, Bull. Am. Phys. Soc. 13, 429 (1968), and to be published.

[9]R. E. Lindquist and A. W. Ewald, Phys. Rev. 135, A191 (1964).

TUNABLE STIMULATED RAMAN SCATTERING FROM CONDUCTION ELECTRONS IN InSb

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We report the observation of tunable stimulated Raman scattering from the spin-flip process of conduction electrons in InSb. With the CO_2 laser at 10.6 μ as the pump, the Raman laser radiation can be tuned from ~11.7 to ~13.0 μ by varying the magnetic field from ~48 to ~100 kG. Raman laser power output of ~1-W peak with linewidth less than 0.05 cm^{-1} has been obtained. Raman conversion efficiency of $\sim 5\times 10^{-4}$ is reported.

We report the first observation of tunable stimulated Raman scattering in the infrared. The Raman scattering process involves electron spin flip[1] in InSb. Tunability is achieved by varying the magnetic field which determines the spacing between the spin sublevels of the Landau levels. Its frequency ω_s varies as $\omega_s = \omega_0 - g\mu_B B$, where ω_0 is the pump frequency, μ_B is the Bohr magne-

ton, B is the magnetic field, and g is the effective gyromagnetic ratio of the electrons in InSb. Spontaneous Raman scattering from this process has been reported earlier in InSb, InAs, and PbTe.[2-4] With pump radiation at 10.5915 μ obtained from a Q-switched CO_2 laser, tunable stimulated Raman emission is observed from ~11.7 to ~13.0 μ by varying the magnetic field from ~48 to ~100 kG. With a pump power of 2 kW inside the crystal, tunable Raman laser power of 1 W is obtained corresponding to a conversion efficiency of $\sim 5 \times 10^{-4}$. This paper represents the first observation of stimulated Raman scattering from a process associated with the mobile carriers in a semiconductor. (See Wolff[5] for an earlier proposal for a similar process).

There have been a number of theoretical papers[1,5] describing various possible processes for inelastic scattering of light by electrons in a magnetic field. Of the three processes ($\omega_S = \omega_0 - 2\omega_c$, $\omega_S = \omega_0 - \omega_c$, and $\omega_S = \omega_0 - g\mu_B B$) theoretically indicated and experimentally observed,[2] the spin-flip process has the largest cross section and the smallest linewidth. Thus, this process is most suitable for stimulated Raman scattering. The following expression[6] gives the Raman gain:

$$g_S = \frac{16\pi^2 c^2 (S/ld\Omega)}{\hbar \omega_S^3 n_p n_s (\bar{n}+1)\Gamma} I, \qquad (1)$$

where g_S is the Raman gain in cm^{-1}, $S/ld\Omega$ is the Raman scattering efficiency in $cm^{-1}\ sr^{-1}$, $n_{p,s}$ are the refractive indices at pump and at Raman-shifted frequencies, respectively. $\bar{n}$ is the Boltzmann factor, Γ is the full width of the spontaneous Raman scattering at half-maximum, and I is the intensity of pump radiation. For spin-flip Raman scattering $S/ld\Omega$ is determined by the Raman scattering cross section per electron, σ, multiplied by the density of electrons, n_e, taking into account the electron statistics of the crystal. σ is expected to be nearly field independent,[1] but the electron statistics make $S/ld\Omega$ for a given n_e dependent on the magnetic field. This has been shown both experimentally[3] and theoretically[7] for $n_e = 3 \times 10^{16}$ in InSb. The experimental results show the spontaneous Raman scattered power increasing by about a factor of 10 as B is increased from 25 to 55 kG,[3] and by another factor of 2 as the field increases further to 100 kG.[8] At $B = 50$ kG, $S/ld\Omega \approx 3 \times 10^{-7}\ cm^{-1}\ sr^{-1}$. Recent NH_3 absorption measurements[9] on the linewidth confirm our earlier estimates of linewidth of $\Gamma = 2\ cm^{-1}$ for the spin-flip process. Thus at $B = 50$ kG the expression in Eq. (1) yields

$$g_S/I = 1.67 \times 10^{-5}\ cm^{-1}/W\ cm^{-2}. \qquad (2)$$

Even though this gain compares very favorably with that obtained for phonons in the visible region,[6] stimulated emission in InSb in the infrared is difficult because of the free-carrier absorption, α, which is ~1.4 cm^{-1} at $B = 0$ and ~8 cm^{-1} at $B = 100$ kG for linearly polarized light with $E \perp B$, propagating normal to B. However, with $I \geq 10^6\ W\ cm^{-2}$, it should be possible to obtain stimulated emission at $B = 50$ kG where $\alpha = 2.0\ cm^{-1}$. (We will consider the exact experimental geometry later in the paper.) It would be harder to observe stimulated Raman scattering at lower magnetic fields because of the drop in the Raman scattering efficiency, while at high magnetic fields the free-carrier absorption will be detrimental.

A repetitively Q-switched CO_2 laser with a diffraction grating inside the laser cavity was used to provide pump power of ~3 kW on a single transition at 10.5915 μ. Apertures in the pump laser cavity assured its operation in the lowest order transverse mode. The laser pulses were 250 nsec wide with a repetition rate of 120 Hz. The pump laser radiation was focused with a 30-cm $f1$ lens into a $n_e = 3 \times 10^{16}\ cm^{-3}$ InSb sample ($T \approx 25$-30°K) in a superconducting solenoid. The sample geometry was $\vec{k}_0, \vec{k}_1 \perp \vec{B}_z$ where $\vec{k}_0, \vec{k}_1$ are the pump and Raman scattered light wave vectors, and $\vec{k}_0 \perp \vec{k}_1$. See the inset in Fig. 3. No reflective coatings were present on the sample. The Raman scattered radiation resonated in a cavity whose length was $l \approx 2.5$ mm and whose mirror reflectivity was 36% as determined by the refractive index of InSb. The InSb sample was ~5 mm long in the $\vec{k}_0$ direction. This is not the ideal geometry for stimulated Raman scattering since the pumped region is a small fraction of the Raman cavity length while the free carrier absorption occurs over the entire length l. A more desirable geometry would be one where $\vec{k}_0$ and $\vec{k}_1$ were collinear. However, the present geometry is convenient for the detection of Raman scattered light below the stimulated threshold. The pump radiation was linearly polarized along $\vec{B}_z$. The Raman scattered radiation was analyzed with a $\frac{3}{4}$-m spectrometer. A Ge:Cu detector was used. An ether absorption cell was used[10] for varying the pump laser intensity.

Figure 1 shows the spin-flip Raman scattered power at $B = 52$ kG ($\lambda = 11.89\ \mu$) as a function of the input pump power. (The spectrometer slits

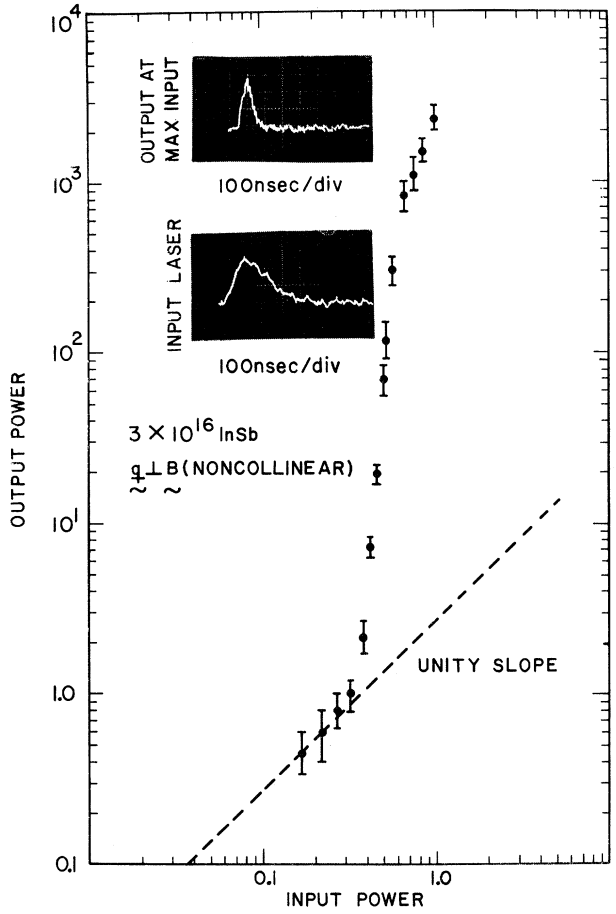

FIG. 1. Variation of the spin-flip Raman scattered output as the pump power at 10.5915 μ is changed, $B = 52$ kG, and the spectrometer is set at 11.89 μ (see text). Input and output scales are in arbitrary units. One unit on the input scale corresponds to peak pulse power of ~2 kW inside the sample of InSb. The maximum output corresponds to a peak pulse power of ~1 W. The inset oscilloscope pictures show the stimulated Raman emission pulse at maximum input power at $B = 52$ kG, and the laser input pulse, respectively (see text for details); $\vec{q} = \vec{k}_0 - \vec{k}_1$.

were kept wide open to have a resolution of 3-4 cm^{-1}.) At low pump power, the spin-flip scattered power varies linearly with the pump power. This region for $P_{in} \lesssim 0.4P_{max}$ is clearly identified as the spontaneous Raman scattering. At $P_{in} \approx 0.4P_{max}$ the Raman scattered power abruptly increases by a factor of 1000 for an input power change of a factor of about 2. This is an unambiguous indication of the onset of stimulated Raman scattering at a threshold of $P_{in} \approx 0.4P_{max}$, which corresponds to a pump power of ~1 kW inside the crystal. The stimulated nature of the spin-flip scattered radiation is also demonstrated by the inset oscilloscope pictures of the laser input pulse and the output pulse at $\lambda = 11.89$ μ (at $B = 52$ kG) taken at maximum input power. The striking difference in the two pulse shapes is in agreement with our conclusion of stimulated emission. The pump pulse is ~260 nsec wide while the Raman scattered pulse is only ~60-70 nsec wide indicating that the spin-flip Raman radiation is stimulated only when the input pulse power exceeds ~0.7 of its peak. Both the input and the Raman scattered pulses were recorded on the same oscilloscope scales (by properly attenuating the pump pulse) in order to remove completely artifacts arising from possible detector saturation. The pulse shapes are consistent with the output-input curve which shows a departure from the unity-slope line at $P_{in} \approx 0.4P_{max}$. The output-input curve was obtained with the use of a boxcar integrator. The output pulses, as seen on the oscilloscope, fluctuated by more than a factor of 5 for $P_{in} \gtrsim 0.4P_{max}$, even though the input pulse variation was less than ~10%. This is not unexpected since even at maximum input power we are only about a factor of 2 above threshold. The boxcar averaging makes the output-input curve look less steep than the actual one, and the experimental curve is not corrected for this source of error. The experimental points are, however, corrected for the difference in the input and the output pulse widths, since the boxcar gate was wider than either one of the pulses. At the maximum input power, estimated Raman scattered power is ~1 W. It is not clear if the tendency towards the saturation of P_{out} as seen on Fig. 1 at the highest input power is real or not. If real, it may arise from the fact that in the focal region of the pump radiation we have rather a small number of electrons ($\sim 5 \times 10^{12}$ electrons, see later for an estimate of volume of the pump beam in InSb) which contribute to the Raman laser output. The spin relaxation time of the conduction electrons in InSb is expected to be of the order of 10^{-9}-10^{-10} sec,[11] which indicates that the spin-flip scattered power should saturate at a level of ~10-100 W for our geometry. We are investigating the effect further.

Figure 2 shows the output spectrum of the Raman-scattered light taken at $P_{in} = 0.3P_{max}$ and at $P_{in} = P_{max}$ for $B = 52$ kG. At the lower input power, we are clearly below the stimulated Raman threshold. The spectrometer trace, taken with a resolution of 0.5 cm^{-1}, shows the spontaneous Raman line centered at $\lambda = 11.89$ μ, having a half-height width of ~2.5 cm^{-1}. From this we estimate a linewidth of ~2 cm^{-1} for spontaneous spin-

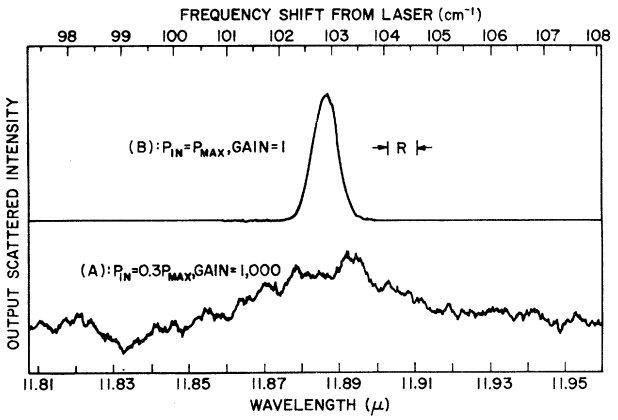

FIG. 2. Spectrometer analysis of the spin-flip scattered light above and below the stimulated emission threshold, showing the narrowing of the emission line under stimulated emission conditions. (Gain on the figure refers to the amplifier gain.)

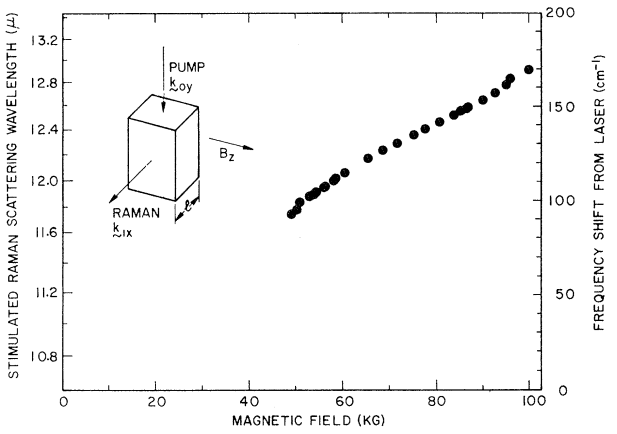

FIG. 3. Tuning curve for the spin-flip Raman laser in the $n_e = 3\times10^{16}$-cm^{-3} InSb sample. (Pump laser is at 10.5915 μ as obtained from a Q-switched CO_2 laser.) The inset shows the experimental geometry for the spin-flip Raman laser.

flip Raman scattering. Curve B in Fig. 2, taken above the stimulated Raman threshold (with the same spectrometer resolution, but with the gain reduced by 1000), shows a significantly narrower line, whose half-height width is no more than the spectrometer resolution. Traces taken at $P_{in} = P_{max}$ with spectrometer resolution of 0.14 cm^{-1} do not show any contribution to the total linewidth from the Raman emission line itself, indicating that above the stimulated Raman threshold the emission linewidth is reduced significantly below the spontaneous linewidth of ~2 cm^{-1}. We estimate the spin-flip Raman laser linewidth to be less than 0.05 cm^{-1}. At the small spectrometer resolution, under the conditions of maximum input power we have seen indications of two very narrow output lines separated by ~0.5 cm^{-1}. The two lines are interpreted as Raman laser oscillation on two adjacent cavity modes. This is seen only when the Raman laser is operating very well at $B = 50$-60 kG where the Raman-scattered power output is maximum. The spectral analysis confirms that stimulated spin-flip Raman scattering is obtained in InSb.

The evidence that the above stimulated Raman emission arises from the electron spin-flip in InSb is shown in Fig. 3, where we see the output wavelength of the spectrally very narrow radiation as a function of B. The Raman emission is stimulated at 48 kG $\lesssim B \lesssim$ 100 kG. Its wavelength varies from ~11.7 to 13.0 μ in agreement with the tunability of the spin-flip Raman process given by $\omega_S = \omega_0 - g\mu_B B$, with the g value of the electrons in InSb varying from about 48 at $B = 0$ to about 35 at $B = 100$ kG. Because the Raman emission line is very narrow, its wavelength can be very accurately determined to about 1 part in 10^5. The biggest error in the tuning curve arises from the fact that the Raman laser will tend to oscillate on the cavity modes which in the present case are separated by ~0.5 cm^{-1} and from the fact that at present we cannot measure the magnetic field very accurately.

The Raman laser output is not constant as its wavelength is tuned from ~11.7 (the lowest $B = 48$ kG where stimulated emission is obtained) to ~13.0 μ (the highest $B = 100$ kG where stimulated emission stops). The lower and the upper magnetic field limits for stimulated emission are not entirely unexpected. These have their origins in the maximum available pump power and the experimental geometry for resonating the Raman radiation. With the Raman cavity length of ~2.5 mm, the single-pass loss for the Raman radiation is calculated to be ~0.5 Np (at $B = 50$ kG). Together with a surface reflection of 36%, we have a total single-pass loss of ~1.5 Np which has to be overcome in order to build up the Raman laser radiation. The calculated gain is given in Eq. (2). Since the gain occurs over only the width of the pump beam which is much smaller than the Raman laser cavity length, the net Raman gain in the cavity is

$$g = g_s(P/\pi r_0^2)2r_0 = g_s(2P/\pi r_0), \qquad (3)$$

where g_s is the gain calculated in Eq. (2), P is the pump power inside the sample, and r_0 is the pump-beam radius. It is not possible to measure

r_0; however, a reasonable estimate of $r_0 \approx 100\ \mu$ gives a net Raman gain of 2.1 Np at the maximum input power of 2 kW. This clearly allows us to obtain Raman laser oscillation at $B = 50$ kG. Since the spontaneous spin-flip Raman scattering efficiency, $S/ld\Omega$, drops very rapidly as the magnetic field is reduced from 55 to 30 kG (as seen in Fig. 24 of Ref. 3) it is reasonable that in the present geometry the Raman laser does not work below $B \approx 45$ kG. Above $B \approx 50$-60 kG, the Raman scattering efficiency goes up by a factor of 2 as B is increased to 100 kG, but the free-carrier absorption goes up by a factor of 3-4, and the stimulated Raman power output at $B = 100$ kG drops by a factor of 20 from its maximum value at $B = 58$ kG. Above $B = 100$ kG stimulated Raman scattering is not obtained which is ascribed to the high free carrier absorption. A different sample geometry may remove some of these restrictions.

In conclusion, we have demonstrated a tunable stimulated spin-flip Raman scattering process arising from conduction electrons in InSb. The Raman laser output of ~1-W peak is tunable from ~11.7 to 13.0 μ by changing the magnetic field from 48 to 100 kG. It may be possible to improve the present conversion efficiency of $\sim 5 \times 10^{-4}$ by increasing the pump power and by shortening the spin relaxation time for the electrons in InSb. The extremely narrow linewidth of 0.05 cm^{-1} together with the high peak and average power makes the spin-flip Raman laser ideally suitable for high-resolution spectroscopy and as a local oscillator in communication systems. Higher magnetic fields together with an improved sample geometry, such as collinear pump and Raman-scattered light, and high-reflectivity coatings on the InSb sample will both increase the tunability of the spin-flip Raman laser and lower its threshold leading to higher conversion efficiencies.

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[1]Y. Yafet, Phys. Rev. 152, 858 (1966).
[2]R. E. Slusher, C. K. N. Patel, and P. A. Fleury, Phys. Rev. Letters 18, 77 (1967).
[3]C. K. N. Patel, Modern Optics (Polytechnic Press, Brooklyn, N. Y., 1967) Vol. XVII, pp. 19-51.
[4]C. K. N. Patel and R. E. Slusher, Phys. Rev. 167, 413 (1968), and 177, 1200 (1969).
[5]P. A. Wolff, J. Quantum Electron. 2, 659 (1966), and Phys. Rev. Letters 16, 225 (1966).
[6]W. D. Johnston, Jr., and I. P. Kaminow, Phys. Rev. 168, 1045 (1968), and 178, 1528(E) (1969), and references cited herein; W. D. Johnston, Jr., I. P. Kaminow and J. G. Bergman, Jr., Appl. Phys. Letters 13, 190 (1968).
[7]V. P. Makarov, Zh. Eksperim. i. Teor. Fiz. Pis'ma Redakt. 55, 704 (1968) [JETP Letters 28, 366 (1969)]; B. S. Wherrett and P. G. Harper, Phys. Rev. 183, 692 (1969).
[8]C. K. N. Patel and K. H. Yang, to be published.
[9]C. K. N. Patel and E. D. Shaw, to be published.
[10]C. K. N. Patel and R. E. Slusher, Phys. Rev. Letters 19, 1019 (1967).
[11]P. A. Wolff, private communication.

LUMINESCENCE SPECTRA OF EUROPIUM CHALCOGENIDES: EuO, EuS, and EuSe†

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Electron-beam–excited luminescence spectra for EuO, EuS, and EuSe show a series of broad and sharp peaks in the energy range from 1 to 4 eV at temperatures between 12 and 300°K. The low-energy broad peaks, corresponding to $4f^7$-$4f^6 5d$ transition, exhibit a redshift, having energies lower than the optical absorption peaks due to a Franck-Condon-like effect. At higher energies, we have observed a series of sharp peaks arising from intra-atomic transitions within the $4f$ configuration in the Eu ions.

In the luminescence spectra of the europium chalcogenides, EuO, EuS, and EuSe, excited by an electron beam, we have found striking structure consisting of a series of broad and sharp peaks, in the photon energy range of 1 to 4 eV, and at temperatures between 12 and 300°K. An electron beam of 10–20 keV and $(1-3) \times 10^{-4}$ A/cm^2, modulated at low frequencies, is focused within a spot of size a few square millimeters on the cleaved surface of nominally pure, single crystals mounted on a cold finger. The emitted luminescence is dispersed by a CaF_2 prism spectrometer, and detected by either S-1 or S-13 photomultiplier dependent upon the photon energy.

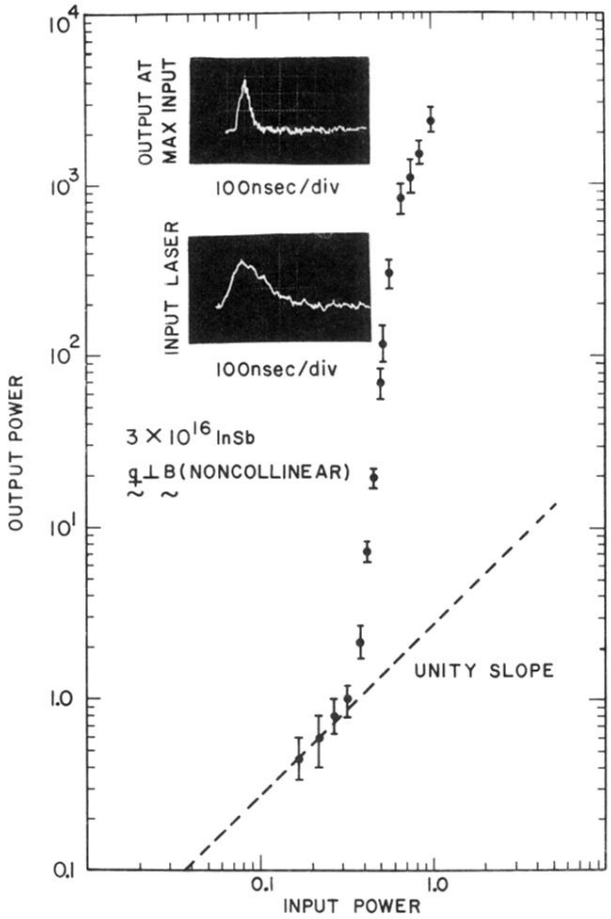

FIG. 1. Variation of the spin-flip Raman scattered output as the pump power at 10.5915 μ is changed, $B = 52$ kG, and the spectrometer is set at 11.89 μ (see text). Input and output scales are in arbitrary units. One unit on the input scale corresponds to peak pulse power of ~2 kW inside the sample of InSb. The maximum output corresponds to a peak pulse power of ~1 W. The inset oscilloscope pictures show the stimulated Raman emission pulse at maximum input power at $B = 52$ kG, and the laser input pulse, respectively (see text for details); $\vec{q} = \vec{k}_0 - \vec{k}_1$.