the carriers' lowest permissible energies resulting in fewer states at the surface. Also, the electrostatic repulsion between electrons in the surface layer may hinder the occupation of the surface states. Our data show that there is no strong p-type inversion layer at the degenerate germanium clean surface. Detailed calculations with which to compare our findings in helping to formulate an accurate model are not yet available.

The authors wish to thank Professor P. Handler for suggesting this experiment and for discussions during the initial phases of these investigations.

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OBSERVATION AND SATURATION OF A MULTIPHOTON PROCESS IN $NdCl_3$

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We have observed intense visible fluorescence (3300 to 9500 Å) and intensity-dependent attenuation at 1.06 μ in single crystals of $NdCl_3$, Nd^{3+}:$LaCl_3$, and Nd^{3+}:$LaBr_3$ using 1.06-μ radiation from a cw Nd-doped yttrium aluminum garnet (YAlG) laser.[1] In this Letter only the measurements on $NdCl_3$ will be discussed.[2]

At low excitation levels, the fluorescence shows a fourth-power dependence on 1.06-μ power; this together with the fact that fluorescence is observed at wavelengths shorter than one-third the laser wavelength indicates that the excitation process involves four laser photons. $NdCl_3$ is transparent at low intensities at the Nd:YAlG laser frequency ν_L because Nd^{3+} has no levels with energy $h\nu_L$ above the ground state; however, the material does have known levels[3,4] (see Fig. 1) which we simply designate as e_2, e_3, and e_4, such that e_2-e_1 and e_4-e_3 are each $2h\nu_L$. These facts about the energy-level scheme suggest that the four-photon process we observe in $NdCl_3$ is a stepwise process involving a double-photon transition ($^4I_{9/2}\rightarrow{}^4G_{7/2}$) followed by another double-photon transition ($^4F_{3/2}\rightarrow{}^4D_{5/2}$). The two double-photon steps each satisfy the selection rules $\Delta S=0$, ΔL, $\Delta J\leq 2$ for an electronic double-photon process.[5,6] In this Letter we present results which clearly indicate that saturation of this multiphoton process in $NdCl_3$ is readily achieved with power levels available from the cw Nd:YAlG laser. To date, two-[7-11] and three-photon[12] absorptions at optical frequencies have been observed only with Q-switched pulsed lasers; here we report the first observation and saturation of a four-photon process with a cw laser.

A schematic of our experimental setup is shown in Fig. 2. The 1.06-μ radiation from the Nd:YAlG laser was focused within the sample of $NdCl_3$ by the 12-mm focal length, $f/4$ lens, L_1. For room-temperature measurements oriented single crystals of approximately 2 mm $\times$2 mm$\times$2 mm were enclosed in evacuated rectangular quartz optical cells, whereas for low-temperature measurements they were mounted in a cold-finger metal Dewar having three optical access windows. Light transmitted through the crystal was collected with lens L_2 and received by thermopile T_2. The incident laser beam was measured with thermopile T_1. Each thermopile was provided with a 1.06-μ narrow-band interference filter. The intensity of the incident beam was varied by means of a calibrated optical attenuator, and the laser was operated at a constant output of 1 W. Observations of the fluorescence were made at right angles to the incident laser beam using a spectrometer and photomultiplier as shown. A Corning 7-57 filter was placed at the output of the laser to keep any visible laser pump light from reaching the sample. A narrow-band dielectric mirror with 99% reflectivity at 1.06 μ was placed on the entrance slit

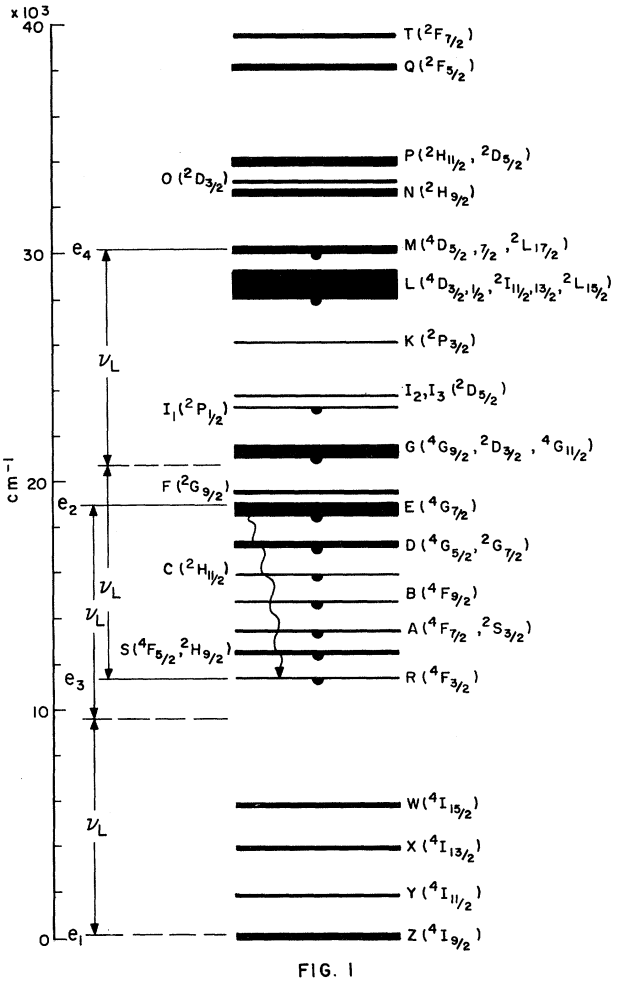

FIG. 1

FIG. 1. Energy levels of trivalent neodymium in the anhydrous chloride. Fluorescent levels are marked with a semicircle.

of the monochromator to remove scattered laser light.

The effectiveness of the 1.06-μ laser light in exciting fluorescence in $NdCl_3$ by multiphoton absorption is evident from the fact that fluorescence groups detected with the monochromator and photomultiplier were 60 dB more intense when excited by the 1-W 1.06-μ laser than they were when excited by a 1-kW Hg lamp. The fluorescence spectrum excited by the laser was identical to the previously known spectrum of these crystals.

The dependence of the intensity of fluorescence upon incident laser power was investigated for a large number of fluorescence groups originating from levels A, B, C, D, E, G, I, L, and M. Figure 3 shows the dependence of the 6600-Å group which originates from the E levels. Similar results were obtained for other fluorescent groups between 3300 and 9500 Å. All groups exhibit a fourth-power dependence on incident laser flux I_0 for fluxes less than ~3 $\times 10^{23}$ photons/cm² sec, and at incident fluxes above 2×10^{24} photons/cm² sec the fluorescence tends to saturate. In Fig. 3 the dependence at 300°K of transmitted 1.06-μ laser flux I on incident flux I_0 is shown for $NdCl_3$. Below about 3×10^{22} photons/cm² sec the crystal is transparent and the transmitted flux is linearly proportional to the incident flux level. Above 2×10^{24} photons/cm² sec the transmitted flux is again linearly proportional to the incident flux

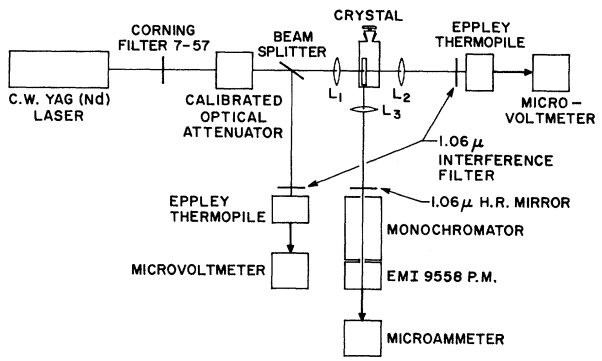

FIG. 2. Schematic of the experimental arrangement.

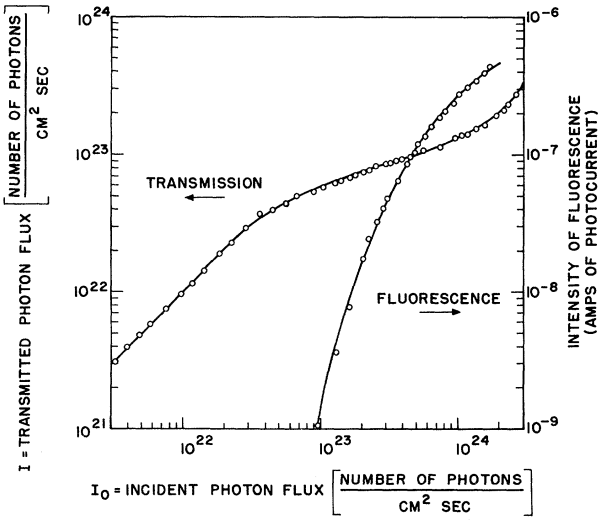

FIG. 3. Dependence at 300°K of transmission and fluorescence upon incident 1.06-μ laser flux for $NdCl_3$. The solid fluorescence curve is calculated from $I_F = (\text{const}\times I_0^4)S^{-1}$, and the solid transmission curve is calculated from Eq. (6) in the text. For each of the solid curves we have used $\sigma_1 = 1.3\times 10^{-44}$ cm⁴ sec, $\sigma_1\sigma_2\rho = 2.1\times 10^{-91}$ cm⁸ sec³, $(\sigma_1 a + \sigma_2 b) = 4.24\times 10^{-47}$ cm⁴ sec², $2\sigma_1\sigma_2 c = 4.5\times 10^{-95}$ cm⁸ sec⁴, and const $= 2.5\times 10^{-101}$ cm⁸ sec⁴ A.

level. In the intermediate incident range of 3×10^{22} to 2×10^{24} photons/cm^2 sec a limiting type of intensity-dependent attenuation is observed.

The above behavior was observed when the laser was polarized parallel as well as perpendicular to the c axis of the $NdCl_3$ crystal. It was observed that the limiting portion of the transmission curve occurred at higher power levels at 10°K than it did at 300°K. The observed dependence on temperature is accounted for if the two-photon absorption of our multiphoton process originates from a Stark level of the ground manifold at 224 cm^{-1}.

As mentioned earlier, on the basis of the energy levels of $NdCl_3$, the process which accounts for our observations is a stepwise four-photon process involving two double-photon transitions. A steady-state solution of the appropriate rate equations for such a process can be shown to predict that the population densities N_2, N_3, and N_4 of levels e_2, e_3, and e_4, respectively, will depend on laser flux I as

$$N_2=[\sigma_1 N\alpha I^2+\sigma_1\sigma_2 N\beta I^4]S^{-1}, \quad (1)$$

$$N_3=[\sigma_1 N\gamma I^2+\sigma_1\sigma_2 N\delta I^4]S^{-1}, \quad (2)$$

$$N_4=[\sigma_1\sigma_2 N\eta I^4]S^{-1}, \quad (3)$$

where S is a saturation denominator given by

$$S=1+(\sigma_1 a+\sigma_2 b)I^2+2\sigma_1\sigma_2 cI^4, \quad (4)$$

N is the density of ions, σ_1 and σ_2 are the cross sections of the two double-photon transitions (e_2-e_1) and (e_4-e_3), respectively, and α, β, γ, δ, η, a, b, and c are constants (not necessarily independent) containing the decay times of the levels e_2, e_3, and e_4. Fluorescence emanating from levels higher than $2h\nu_L$ above the ground manifold will be fed only by the N_4 population and will have an intensity proportional to N_4. Similarly, fluorescence from levels lower than $2h\nu_L$ will have an intensity proportional to a linear sum of either N_2 and N_4 or of N_2, N_3, and N_4. With regard to transmission through the medium, the change in beam flux with distance is given by

$$dI/dx=-n[\sigma_1 NI^2+\sigma_1\sigma_2 N\rho I^4]S^{-1}, \quad (5)$$

where ρ, as for the N's, contains the decay times of the levels concerned and n is the refractive index of the medium. Upon integration of (5), the dependence of transmitted flux I upon incident flux I_0 in a length l of the medium is given by

$$\frac{2c}{N\rho}[I-I_0]-\frac{1}{\sigma_1 N}\left[\frac{1}{I}-\frac{1}{I_0}\right]+\frac{[\rho(\sigma_1 a+\sigma_2 b)-\sigma_2\rho^2-2\sigma_1 c]}{\sigma_1 N\rho(\sigma_2\rho)^{1/2}}\times\{\tan^{-1}[I(\sigma_2\rho)^{1/2}]-\tan[I_0(\sigma_2\rho)^{1/2}]\}=-nl. \quad (6)$$

The result of fitting Eq. (6) to our experimental transmission data on $NdCl_3$ is shown by the solid curve in Fig. 3. Using the values of $l=3\times10^{-2}$ cm, $n=1.8$, and $N=10^{22}$ cm^{-3} appropriate to our $NdCl_3$ experiments, a best fit was obtained with the constants given in the figure caption. A value for σ_1 of 1.3×10^{-44} cm^4 sec was thus determined. Using values of the lifetime-dependent constants as calculated from measured lifetimes[13] of the levels involved, we also determined that $\sigma_2=1.6\times10^{-41}$ cm^4 sec. An attempt at a theoretical estimate of σ_1 from Kleinman's[14] simplified formula, taking the width of the final state ($^4G_{7/2}$) equal to 6×10^{12} sec^{-1}, $\nu_L=2.8\times10^{14}$ sec^{-1}, and the oscillator strength of the intermediate state equal to unity, yielded σ_1(calc)$=4.6\times10^{-47}$ cm^4 sec. This is considerably smaller than our observed value, and the disparity is undoubtedly due to the fact that in Kleinman's expression it is assumed that only a single intermediate state at very high energy connects the initial and final states. Obviously a careful sum over all possible intermediate states of $NdCl_3$ will be necessary to account for our measured value of σ_1. The reason that the measured σ_2 is larger than σ_1 is probably related to the fact that, for σ_2, the intermediate states are in closer proximity to the initial and final levels of the two-photon transition.

From the above values of σ_1 and σ_2 and values of α, β, γ, and δ calculated from the lifetime measurements,[13] we find that over the range of our present fluorescence observations the terms containing I^2 in the numerators of Eqs. (1) and (2) are negligible compared to the I^4 terms, and thus the intensity of observed fluorescence I_F versus incident flux I_0 should be given by $I_F=(\text{constant}\times I_0^4)S^{-1}$. As shown in Fig. 3, this is exactly what is observed experimentally for the multiphoton-excited fluorescence in $NdCl_3$.

In the present Letter we have demonstrated that in $NdCl_3$, multiphoton spectroscopy can

be conducted with a cw Nd:YalG laser of moderate power and that in this material a stepwise four-photon process involving two double-photon transitions is operative.

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TEMPERATURE DEPENDENCE OF HEAT-PULSE PROPAGATION IN SAPPHIRE

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Results of heat-pulse measurements between 4 and 54°K are reported for sapphire and show that the propagation is ballistic below 18°K and diffusive above 40°K. In the intermediate range, the propagation is a superposition of the two.

Data have been reported earlier on the propagation of heat pulses in quartz and sapphire at 3.8° and ~8.5°K.[1] Other reports have since appeared on the propagation of heat pulses in sapphire and other solids.[2-5] Heat-pulse data, taken as a continuous function of temperature, can give information on phonon-phonon scattering phenomena. A wave-like propagation of heat pulses (second sound) may result from a high rate of normal-process events compared to all other scattering events.[6] The experiment in solid helium[4] has been interpreted as evidence of second sound. We wish to report results on heat-pulse propagation in sapphire. The material is particularly well suited for this investigation since its thermal conductivity is high and its elastic properties are well known. Also, the acoustic velocity is quite isotropic and the singleness of the crystals can be assured. We have observed the superposition of several modes of thermal transport but none corresponding to second sound. It appears that if indeed second sound has been observed in solid helium, the phenomenon is not as general as recent theory predicts.[7]

We have extended our earlier low-temperature work as a continuous function of temperature up to 54°K. This is well above the temperature (~30°K) of the thermal conductivity maximum,[8] the temperature near which a maximum number of N-process compared with U-process collisions should occur, and therefore near which second sound is most likely to occur.

The findings of the present experiment are that (1) the observed onset time of the arriving heat pulses for the longitudinal phonons is essentially constant for the temperature range 4-40°K and for the transverse phonons this time is almost constant, increasing by only ~5% over this temperature range; (2) as the temperature increases the amplitude of the sharp transverse pulse relative to the longitudinal pulse decreases; also by 18°K appreciable phonon-phonon scattering is present which gives rise to an additional diffuse maximum at times substantially later than either the acoustic-energy transport time or that expected for second sound; (3) from 40 to 54°K, no observable heat arrives at the acoustic velocity, but