absorption at the room temperature end of the transducer. The least-square fits to the Eu^{2+} spectra showed one single phase at all T and were successful even very close to T_c, in contrast to our findings for either EuS or EuSe. No Eu metal could be detected and trivalent Eu impurities were less than 1%. The narrow linewidths indicate an electronic spin relaxation time that is sufficiently short to produce a true time-averaged field at the nucleus. Only close to T_c the lines broaden as a result of short-range-order spin fluctuations.

[8]P. Heller and G. Benedek, Phys. Rev. Lett. 14, 71 (1965).

[9]S. von Molnár and T. Kasuya, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970*, edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U. S. AEC Division of Technical Information, Springfield, Va., 1970), p. 233.

[10]S. von Molnár and M. W. Shafer, J. Appl. Phys. 41, 1093 (1970).

[11]S. S. Bashkirov and G. Y. Selyutin, Phys. Status Solidi 26 253 (1968)

[12]V. L. Moruzzi and D. T. Teaney, unpublished.

[13]F. Lévy, Phys. Kondens. Mater. 10, 71 (1969).

[14]J. D. Axe, J. Phys. Chem. Solids 30, 1403 (1969).

Stimulated Emission from the Excitonic Molecules in CuCl

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We report observation of efficient stimulated emission (gain $\sim 10^4$ cm^{-1}) from recombination of excitonic molecules. This emission is obtained near 3.16 eV (3920 Å) in optically excited CuCl crystals and shown to be stimulated by use of a recently described technique employing a variable excitation length. These results in CuCl point out the importance of excitonic molecules in intrinsic stimulated-emission processes in semiconductors.

We report the observation of efficient stimulated emission from recombination of excitonic molecules. These molecules represent the lowest intrinsic energy state in many crystals at high excitation levels, and it might be expected that excitonic molecule recombination (EMR) will play an important role in stimulated emission processes. It has previously been speculated,[1] but then discounted,[2] that EMR could be a fundamental recombination route for intrinsic stimulated emission in many semiconductors.[3] The observations described here were made on optically excited CuCl crystals and represent the first demonstration of *stimulated* excitonic molecule recombination. Spontaneous emission due to EMR in CuCl near $\lambda = 3920$ Å had been previously established[4,5] with the reported molecular binding energy being $\simeq 44$ meV.[5] CuCl is an ideal crystal in which to investigate stimulated emission from excitonic molecule recombination. It is a zinc-blende semiconductor with a band gap in the uv, the lowest exciton absorption peak occurrring at 3.207 eV at 4.2°K.[6] Three sharp absorption lines of the exciton series have been observed and found to be not hydrogenically spaced. This results because the exciton is deeply bound (binding energy 190 meV and Bohr radius 7 Å) and the usual effective-mass theory breaks down. Low-intensity photoluminescence spectra[7] show the usual bound-exciton lines common to wide-band-gap semiconductors. At very high exciting intensities, a new peak appears[4,5] at 3.164 eV, about 44 meV below the free-exciton energy, and it has been identified as exciton-molecule recombination radiation. In this paper, we discuss new studies of this radiation.

The EMR mechanism is an Auger process whereby one of the excitons is scattered into either the $n = 1$ or higher state of the free exciton while the other is simultaneously scattered down on the polariton curve. A schematic diagram of the EMR process is shown in Fig. 1. The photon is shifted down in energy from the absorption peak of the $n = 1$ exciton by the binding energy of the molecule ($R_m = 44$ meV in CuCl)[5] if the terminal state of the surviving free exciton is $n = 1$. This photon energy represents the high-energy threshold for the EMR radiation. For recombining molecules with large crystal momenta K, the radiation will appear with energies at and below this threshold because of the difference in the dispersion of the molecule and the free exciton, as seen in Fig. 1. The momentum-conserving properties of the Auger process allow radiation to arise even from molecules with large crystal momenta so that the number of initial states that may participate is much larger than for ordinary exciton recombination. Thus there is good rea-

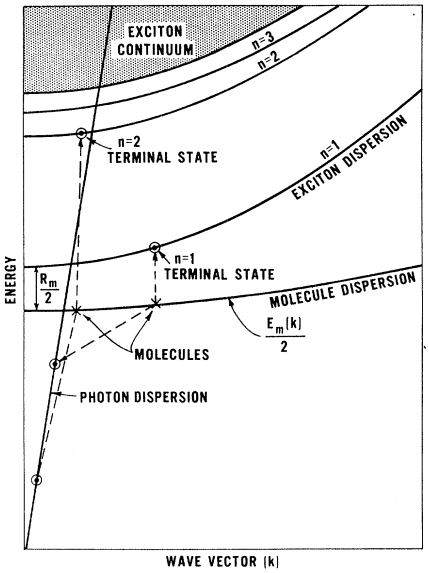

FIG. 1. Dispersion curves for the photon, exciton, and excitonic molecule. The excitonic molecule energy $E_m(k)$ has been divided by 2 in order to be represented conveniently with the exciton dispersion curves. The arrows illustrate two possible decay mechanisms for an excitonic molecule which decays into a photon plus a free exciton in either the $n=1$ or $n=2$ state.

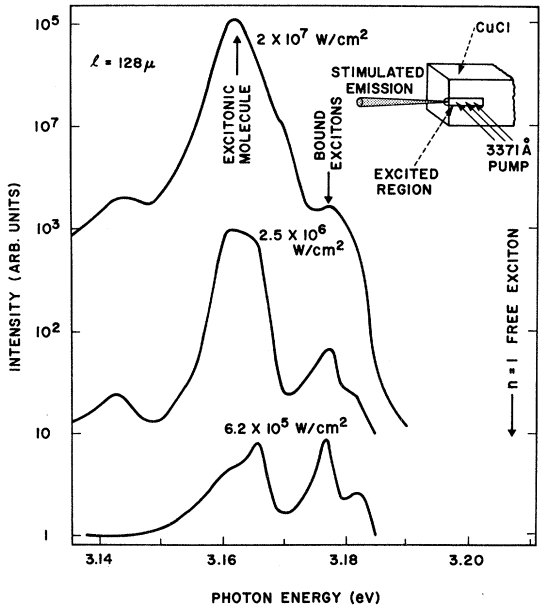

FIG. 2. High-intensity photoluminescence spectra of CuCl at 2°K for three pump powers (indicated by the numbers associated with each curve). The inset illustrates the geometry used for measurements. Note: l is the length of the excited region.

son to believe that EMR can in general show stimulated emission.

Crystals of CuCl are hygroscopic and quite soft, so that the standard technique for demonstrating stimulated emission (fabrication of an optical cavity and the observation of actual laser action) would involve considerable effort, and failure to observe laser action would not prove that the EMR process does not exhibit gain. To eliminate this problem, the stimulated emission spectra and gain in CuCl were measured using a recently described gain-measurement technique.[8] The method is indicated schematically in the inset in Fig. 2. A rectangular beam of pump light from a nitrogen laser (3371 Å and ~10^5 W) of width W (≈20 μm) and variable length l (0-100 μm) is focused on the face of the sample near an edge. Light which originates in and passes through the excited region of the crystal and out the edge is dispersed by a monochromator and detected by a fast photomultiplier. This light will have a dependence on the length of excitation of the form[8]

$$I = I_s[\exp(gl) - 1]/g, \quad (1)$$

where I_s is the spontaneous luminescence intensity and g is the net optical gain (i.e., total gain −loss). Hence, a *superlinear* (exponential if $gl > 1$) dependence of I on l is a direct indication of gain and the presence of stimulated emission.

The CuCl samples, grown[9] by a gel diffusion technique, were single crystals in the form of tetrahedra with several as-grown faces suitable for photoluminescence studies. An HCl etch was used to assure clean, undecomposed CuCl surfaces just prior to immersion in liquid helium for measurements.

The stimulated emission spectrum of CuCl at 2°K measured for various excitation intensities is given in Fig. 2. The spectrum shows two distinct sets of features: a large peak near 3.16 eV and a doublet near 3.18 eV. The former of these has been previously[4,5] identified as excitonic molecule recombination radiation. The evidence[5] for this interpretation was based on two facts: the approximate square-law power dependence of the observed peak intensity, and the emitted photon energy which is in agreement with the theory[3] for excitonic molecules. Our results are in agreement with these facts for sufficiently low pump powers and the corresponding geometry, i.e., observation of luminescence from the front surface of the sample. For the geometry shown in Fig. 2, however, it is seen that the intensity of the 3.16-eV peak increases by more than a factor of 100 for a factor of 4 increase in pump power

density. This large increase is suggestive of gain in the molecule recombination. (The doublet near 3.18 eV, which has been attributed to bound excitons,[10] has only slightly greater than linear dependence on power and will not be discussed here.)

A positive identification of stimulated emission and gain on the 3.16-eV peak is obtained by studying the luminescence intensity as a function of excitation *length*. The results of such a study are shown in Fig. 3, which is a plot of emission intensity at 3.166 eV versus excitation length for four different pump powers. These curves all show a linear portion extending over about two orders of magnitude in intensity at the shorter excitation lengths. According to Eq. (1), a linear region in a semilog-plot is a direct indication of the existence of gain. These results thus conclusively demonstrate the existence of stimulated excitonic molecule recombination in CuCl. The departure from linearity in the curves of Fig. 3 at longer excitation lengths is to be expected because of saturation effects.[11] The magnitude of the gain can be obtained by measuring the slope of the linear region of the curve, and values for various pump powers are listed in Fig. 3. In selected samples, peak gains of the order of 10^4 cm^{-1} have been observed for 2×10^7-W/cm^2 pump power. Such gains are more than 2 times larger than in GaAs under similar conditions.[8]

The gains listed in Fig. 3 have a nearly linear dependence on pump power. However, it has been observed that in some samples the gain varies quadratically with pump power at low power levels, then becomes linear at high pump intensities. A similar effect has been observed in the spontaneous EMR luminescence intensity.[4,5] Such a correlation is reasonable since the spontaneous and stimulated emission are related by the Einstein coefficients. As pointed out by Haynes,[12] the quadratic dependence is easily understood in terms of the probability that two excitons will collide and form a molecule. At low exciton densities the probability is proportional to the square of the exciton density and hence the square of the pump power. At high exciton densities the time required for formation of a molecule becomes short compared to the low-density exciton lifetime, and an equilibrium is established where the rate of molecule formation is proportional to the first power of the pump intensity. A detailed solution of the rate equations involved in the formation of excitonic molecules has recently been given.[13]

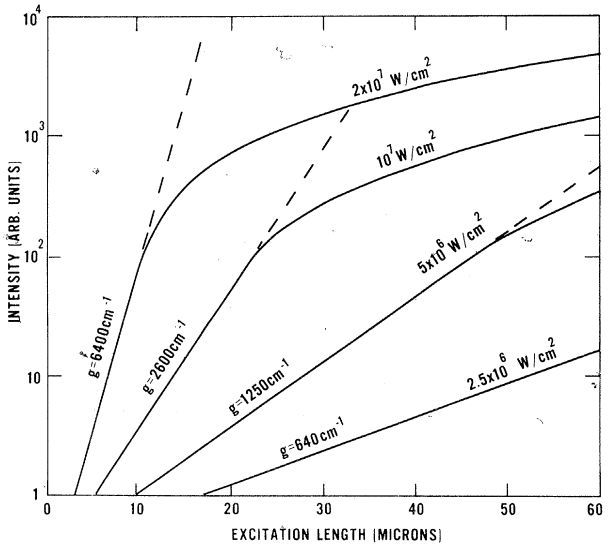

FIG. 3. Emission intensity for EMR radiation [λ = 3915 Å (3.166 eV)] as a function of excitation length for four different pump powers. The gain g, as obtained from the linear portion of each curve on this semilog plot, is given for each pump power.

The large optical gain of the stimulated EMR process in CuCl can be attributed to a number of factors related to the large excitonic molecule binding energy. The EMR emission is separated from the exciton absorption by this large binding energy and thus falls in a relatively low-loss region of the spectrum. The binding energy is large enough so that thermal dissociation of the molecule is unlikely. In addition, this binding energy is sufficiently larger than that of a bound exciton so that the molecule cannot be readily dissociated at impurity sites. Hence the principal decay mechanism available to the molecule is radiative.[14] Further, the recoiling free exciton can absorb momentum during the radiative decay and all the molecules can participate in the gain process. Therefore the excitonic molecule is an intrinsic excitation which can give rise to efficient stimulated emission.

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[1]C. Benoit a la Guillaume, J. M. Debever, and F. Salvan, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Brown University, 1967*, edited by D. G. Thomas (Benjamin, New

York, 1968), p. 669.
[2]D. Magde and H. Mahr, Phys. Rev. B 2, 4098 (1970).
[3]The excitonic molecule may not be a stable entity in all materials. See R. R. Sharma, Phys. Rev. 170, 770 (1968); R. K. Wehner, Solid State Commun. 7, 457 (1969).
[4]A. Mysyrowicz, J. B. Grun, R. Levy, A. Bivas, and S. Nikitine, Phys. Lett. 26A, 615 (1968).
[5]J. B. Grun, S. Nikitine, A. Bivas, and R. Levy, J. Lumin. 1,2, 241 (1970); H. Souma, T. Goto, T. Ohta, and M. Ueta, J. Phys. Soc. Jap. 29, 697 (1970).
[6]S. Nikitine, J. Ringeissen, M. Certier, C. Wecker, S. Lewonczuk, J. C. Merle, and C. Jung, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970,* edited by S. P. Keller, J. C. Hansel, and F. Stern, CONF-700801 (U. S. AEC Division of Technical Information, Springfield, Va., 1970), p. 196.
[7]S. Nikitine and J. Ringeissen, Proc. Phys. Soc., London 26, 171 (1965).
[8]K. L. Shaklee and R. F. Leheny, to be published.
[9]A. F. Armington and J. J. O'Connor, J. Cryst. Growth 3, 367 (1968).
[10]M. Certier, C. Wecker, and S. Nikitine, J. Phys. Chem. Solids 30, 2135 (1969).
[11]Such saturation effects have been observed in many materials and are a consequence of the recombination dynamics.
[12]J. R. Haynes, Phys. Rev. Lett. 17, 860 (1966).
[13]R. S. Knox, S. Nikitine, and A. Mysyrowicz, Opt. Commun. 1, 19 (1969).
[14]Knox *et al.* (Ref 13) assumed negligible radiationless decay of excitonic molecules and still calculated results in agreement with experiments in CuCl (Ref. 5).

Observation of Nonextremal Fermi-Surface Orbits in Bulk Bismuth*

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Using giant quantum oscillations in the attenuation of ultrasound, we have observed nonextremal areas of the electron Fermi surface of bismuth. The giant oscillations occur simultaneously with oscillations due to extremal areas, and both the periods and the general shape of these oscillations can be explained by the theory of Gurevich, Skobov, and Firsov.

We have observed *nonextremal* Fermi-surface orbits by means of giant quantum oscillations in the attenuation of ultrasound in bismuth. The possibility of seeing such orbits in metals and semimetals in a magnetic field was first predicted by Gurevich, Skobov, and Firsov[1] in 1961. Considering the problem of the absorption of a single acoustic phonon by an electron which remains on the same Landau level, they found several interesting features of the acoustic attenuation. One of the properties of these "giant quantum oscillations" is that when the phonon wave vector $\vec{q}$ is nearly perpendicular to the magnetic field $\vec{H}$, the orbits of the electrons responsible for acoustic attenuation are displaced from the extremal Fermi-surface orbit by an amount which depends on the angle between $\vec{q}$ and $\vec{H}$. It should thus be possible to study *any* cross section of the Fermi surface by varying the relative orientation of $\vec{q}$ and $\vec{H}$, a property unique to this type of acoustic attenuation. Giant quantum oscillations have been seen in several materials, and many features of the theory have been confirmed,[2] but there have been no unambiguous measurements of nonextremal Fermi-surface areas.[3,4] When $\vec{q}$ is nearly normal to $\vec{H}$, the attenuation versus magnetic-field curves $\alpha(H)$ become complex, but the periods found in previous experiments correspond to extremal areas.[4,5] We report here the first observation of giant quantum oscillations due clearly to nonextremal orbits. They occur simultaneously with oscillations due to extremal orbit electrons in the vicinity of $\vec{q}$ normal to $\vec{H}$. The resulting Fermi-surface areas agree with the theory of Gurevich, Skobov, and Firsov,[1] assuming an ellipsoidal-parabolic model for the electrons.

The sample was a 1-cm cube spark cut from a single-crystal boule grown by the Czochralski method from 99.9999%-pure bismuth. Resistivity ratio measurements made on small ($15\times1\times1$ mm^3) bars cut from the same boule yielded values of $\rho(300°\mathrm{K})/\rho(4.2°\mathrm{K})\approx230$. A conventional pulse-transmission method was used for the ultrasonic measurements, with gating circuits monitoring the amplitude of the first transmitted pulse. Longitudinal sound waves at 185 MHz were generated by resonant quartz transducers glued to the sample. All measurements were made at a temperature of 1.5°K. The orientation of the sample in the Dewar could be varied by a gear-driven sample holder and rotatable magnet, with an accuracy of about 0.1°. The relative orientation of $\vec{q}$ and $\vec{H}$ was determined by using