Double-Carrier Injection and Negative Resistance in CdS

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Light-sensitive, negative-resistance characteristics, arising from double-carrier injection, have been observed in selected CdS single crystals. The double injection, occurring at Ag and In contacts, is accompanied by relatively intense light emission (green edge fluorescence) even at low injection levels (field strengths often less than 10 V/cm) and the emission is observed largely in the neighborhood of the positive Ag electrode. After appropriate light stimulation of these crystals, pronounced and reproducible negative resistance and semiconductor "regimes," as well as "current oscillations," have been observed at 4.2°K; negative resistance and low-injection-level, space-charge-limited current regions ($I \propto V^2$) have been observed at 77°K. Negative resistance has been observed at low-field strengths (<50 V/cm) in optically stimulated samples; no direct evidence of breakdown effects was observed in unstimulated samples up to a few kV/cm. In terms of Lampert's double-injection (semiinsulator) model, injection-level-dependent hole lifetimes are indicated at 4.2°K; also, optical-stimulation, level-dependent I–V characteristics are indicated at 4.2°K. The I–V characteristics are discussed in terms of Lampert's theory, as well as a breakdown-induced injection theory due to Steele, Ando, and Lampert. A previously proposed mechanically excited emission model, due to Warschauer and Reynolds, is invoked to explain a possible mechanism for double injection in these unusual crystals.

INTRODUCTION

RECENT interest in negative-resistance phenomena in semiconductors has arisen largely as a consequence of its apparent connection with junction laser action; moreover, negative resistance was recently predicted in a double-injection, semi-insulator theory due to Lampert.[1] In particular, considerable attention has recently been focused on the problem of double injection, negative resistance, recombination radiation, and laser action in Te- and Zn-doped GaAs junctions.[2–5] Stafeev[6] has previously predicted and presented experimental evidence for a type of negative resistance in certain Ge diodes, and other investigators have observed negative-resistance regions in the current voltage characteristics of several materials. Melngailis and Rediker[7] have confirmed Stafeev's theory in InSb at low temperature; Holonyak *et al.*[4] have, in principle, recently confirmed Lampert's theory with the observation of double-carrier injection and light-sensitive negative resistance in GaAs, Si, and Ge semiinsulator junctions at room temperature. Van Ruyven and Th. Adriaens[8] have observed temperature-dependent, negative-resistance characteristics in Ge diodes (plastically deformed p-n junctions) due, apparently, to "good" double-carrier injection, while Ryuzan[9] has previously reported negative resistance in plastically deformed Ge junctions. Steele, Ando, and Lambert[10] (hereafter referred to as SAL) have recently developed a theory and reported experimental evidence for field-driven, negative-resistance characteristics in p- and n-type Ge diodes under the conditions of contact breakdown (avalanche-break-down, double-injection-induced negative resistance). In another recent paper,[11] further experimental arguments have been presented on the mechanism of breakdown-induced negative resistance.

Smith[12] has previously reported a "hysteresis" in the dc current-voltage characteristics of near-insulator CdS crystals, as have others in insulating crystals. Smith has interpreted the hysteresis (sharp rise and fall of current in the I-V curves) as the onset of double injection: hole injection is proposed to arise from a "formed patch" (high-field region) at the anode and electrons are injected from an ohmic cathode. He further asserts that double injection (presence of both holes and electrons in the crystal) is inferred from the observation of field-induced recombination radiation. Interestingly, Smith's I-V characteristic curve at 77°K shows a pronounced singularity at a relatively high voltage and low current which would seem to suggest contact breakdown. Although Smith does not specifically call the singularity in his I-V curve[12] a region of negative resistance, Lampert has subsequently inferred[1,10] that such is the case; in principle, at least, Smith's observation is probably more nearly akin to the SAL observations[10] in Ge, namely

[1] M. A. Lampert, Phys. Rev. **125**, 126 (1962), and Proc. IRE **50**, 1781 (1962).
[2] R. N. Hall, G. E. Fenner, J. D. Kingsley, T. J. Soltys, and R. O. Carlson, Phys. Rev. Letters **9**, 366 (1962).
[3] M. I. Nathan and G. Burns, Appl. Phys. Letters **1**, 89 (1962).
[4] N. Holonyak, S. W. Ing, R. C. Thomas, and S. F. Bevacqua, Phys. Rev. Letters **8**, 426 (1962).
[5] M. I. Nathan and G. Burns, Phys. Rev. **129**, 125 (1963).
[6] V. I. Stafeev, Fiz. Tver. Tela **1**, 841 (1959); **3**, 2513 (1961) [translations: Soviet Phys.—Solid State **1**, 763 (1959); **3**, 1829 (1962)].
[7] I. Melngailis and R. H. Rediker, J. Appl. Phys. **33**, 1892 (1962).
[8] L. J. Van Ruyven and W. H. Th. Adriaens, Phys. Letters **3**, 109 (1962).
[9] O. Ryuzan, J. Phys. Soc. Japan **16**, 2177 (1961).
[10] M. C. Steele, K. Ando, and M. A. Lampert, J. Phys. Soc. Japan **17**, 1729 (1962). In 1961, Lampert and Rose [Phys. Rev. **121**, 26 (1961)] gave a one-dimensional treatment of the theory of double injection; more recently, Hirota, Tosima, and Lampert [J. Phys. Soc. Japan **18**, 535 (1963)] have treated the two-dimensional problem of double injection in a constricted semiconductor.
[11] K. Ando, M. C. Steele, and M. A. Lampert, J. Phys. Soc. Japan **18**, 591 (1963).
[12] R. W. Smith, Phys. Rev. **105**, 900 (1957).

avalanche-breakdown, double-injection induced negative resistance, arising from breakdown of one of the contacts. Komiya *et al.*[13] have also observed negative characteristics in the *I-V* curves of high-resistivity CdS samples (room temperature) but they do not attribute the proposed hole injection to a "formed patch" region and they interpret the negative resistance as arising from both electron multiplication (impact ionization) and thermal destruction of the crystal in microscopic regions.

As one might expect, current oscillations have frequently been observed in diodes having negative-resistance characteristics (dc applied potential). Current oscillations in the negative-resistance region of *n*- and *p*-type Ge diodes were reported by SAL[10]; Cardona and Ruppel[14] previously reported such oscillations in Ge diodes but did not observe negative resistance characteristics. Photocurrent oscillations have been observed by several investigators in high resistivity CdS,[15] ZnSe,[16] and GaAs.[17]

The experiments reported here were undertaken primarily to investigate the current-voltage characteristics of selected CdS crystals that show the phenomena of mechanically excited edge emission and conductivity "storage effects." The phenomena and the crystals that show it are hereafter referred to as "tap-effect" and "tap" crystals, respectively. The properties peculiar to these selected single crystals have been previously reported[18–20] and there is every reason to believe that they are significantly different, in both optical and electrical properties, from the CdS crystals used in previous investigations of current-voltage characteristics.[12,13] We have recently observed negative-resistance "regimes" (light-sensitive) in CdS "tap" crystals at low temperature. It is believed that the observed negative characteristic arises from double-carrier injection in a trap-filled semi-insulator, although it may be that double injection into the bulk results from breakdown effects. The purpose of this paper is to report the observed negative resistance, as well as associated "current oscillations," to discuss the negative resistance and double injection in terms of Lampert's model,[1] as well as the SAL theory,[10] and to propose an interpretation for the double injection in terms of a previously proposed energy model for mechanically excited emission.[18]

EXPERIMENTAL

The crystals used in these experiments were grown from the vapor phase by a method due to Greene *et al.*[21] Greene[22] has previously pointed out that there is reason to believe that the CdS "tap" crystals are relatively impure. It is now known that the "tap" crystals are fortuitously "doped" (appreciably) with Group I elements and we are reasonably sure that the "tap-effect" is due to impurities. The impurity problem is currently being investigated. All of the samples were essentially rectangular parallelepipeds, cleaved from larger pieces, and the electrodes were applied to opposite faces (freshly etched or cleaved). In the several samples investigated, anode-cathode spacings ranged from about 5 mm to somewhat over 1 cm, e.g., crystal No. 2 was 1 cm thick. The maximum applied field for this crystal was less than 300 V/cm, since the applied potential ranged from 0 to less than 300 V. Ag was always used for the anode, in most cases, Ag-print circuit paint (air dried). Indium solder (ultrasonically soldered) was used for the cathode. In addition to the circuit paint, we have found that sputtered, electroplated, and thermally evaporated Ag electrodes work equally as well. We have also recently found that a baked-on, epoxy-resin Ag makes a good injecting contact and is mechanically stronger than the circuit paint at low temperatures.

The samples were cooled by immersion in either liquid nitrogen or liquid helium. Sample temperatures were not monitored during a current-voltage measurement and it is assumed that there was no appreciable temperature change as a consequence of ohmic heating.

In all cases applied potentials, rarely greater than 200 V at 77°K and never greater than 400 V at 4.2°K, were supplied by either a regulated dc power supply or batteries. At 77°K, sample current and voltage drop were measured directly with meters; at this temperature, an electronic current limiter[19] (by means of which it was possible to vary the applied potential) was used in series with the sample, primarily to retard or control a self-stimulation process that will be discussed later. At 4.2°K, the crystal voltage drop and current signal were fed into the *x* and *y* inputs, respectively, of a fast dc oscilloscope (Tektronix 536). The applied potential sweep frequency generally had to be less than 60 cps in order to obtain a good negative characteristic trace on the scope. Electronic current-limiting techniques were not used at 4.2°K and the crystal current suffered no

[13] H. Komiya, S. Ibuki, and H. Yamashita, *Luminescence of Organic and Inorganic Materials* (John Wiley & Sons, Inc., New York, 1962), pp. 523–536.
[14] M. Cardona and W. Ruppel, J. Appl. Phys. **31**, 1826 (1960).
[15] S. H. Liebson, J. Electrochem. Soc. **102**, 529 (1955); R. H. Bube and L. Barton, RCA Rev. **20**, 564 (1959).
[16] R. H. Bube and E. L. Lind, Phys. Rev. **110**, 1040 (1958).
[17] J. Blanc, R. H. Bube and H. E. MacDonald, J. Appl. Phys. **32**, 1666 (1961).
[18] D. M. Warschauer and D. C. Reynolds, Phys. Chem. Solids **13**, 251 (1960).
[19] C. W. Litton and D. C. Reynolds, Phys. Rev. **125**, 516 (1962).
[20] A CdS "tap" crystal is a selected single crystal that can be mechanically excited to green edge fluorescence, after thermal or optical stimulation at low temperature—such crystals will remain stimulated in a totally darkened room. Thermal stimulation is accomplished by cooling a crystal to 77°K (or lower) in complete darkness, while optical stimulation is accomplished by irradiating the crystal with light after cooling. Warschauer and Reynolds have shown that the threshold for optical stimulation is approximately 6900A, or 1.75-eV photons. They have also established that stimulated "tap" crystals can be excited to edge fluorescence by irradiating them with light of at least 0.75-eV photon energy.
[21] L. C. Greene, D. C. Reynolds, S. J. Czyzak, and W. M. Baker, J. Chem. Phys. **29**, 1375 (1958).
[22] L. C. Greene (private communication). This speculation arose mainly from a consideration of relative purities of CdS powders from which the crystals were grown.

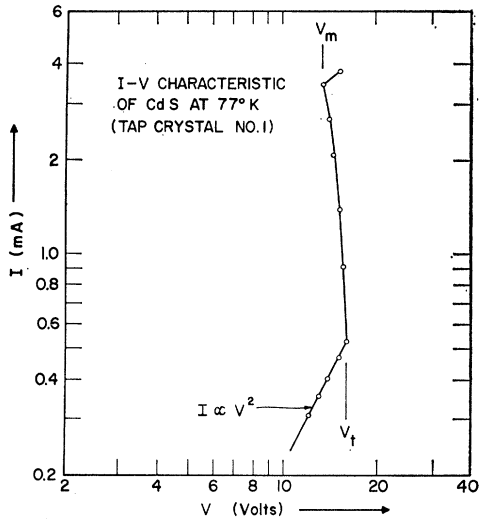

FIG. 1. Current-voltage characteristic of CdS "tap" crystal at 77°K. The applied potential was supplied by a dc power supply with a current limiter (Ref. 19) in series with the crystal.

limitations during a sweep, save that due to a small series load resistor. The oscilloscope was calibrated and the initial crystal current and voltage levels were determined before each *I-V* curve was traced out by the sweep potential. Before each *I-V* measurement at 4.2°K, the sample was stimulated with light (stimulated to a level less than its maximum level of "stored" conductivity) and then completely shielded to preclude further stimulation by ambient light.

RESULTS AND DISCUSSION

A. Previous Observations

One of the more interesting properties of the CdS "tap" crystals is a conductivity "storage effect," and at 77°K, some of these crystals show a conductivity increase of more than 10 orders of magnitude when exposed to stimulating radiation.[18,19] Upon removal of the stimulating light, dark resistivities are quite low and the high conductivity will remain at a constant value, indefinitely, provided the thermal and optical environment is not changed. In general, a crystal may be cooled to any temperature (77°K and below) in total darkness after which the crystal can be stimulated to any desired level of conductivity (up to a maximum or saturation level) by simply exposing it to stimulating light for different periods of time. Suffice is to say that there is an "integrating effect" in the light-induced stored conductivity. The maximum level of stored conductivity at 4.2°K is not quite as high as the corresponding maximum at 77°K in a given crystal; also, the maxima vary appreciably from crystal to crystal.

Electric-field-induced emission has previously been reported[19] in optically stimulated CdS "tap" crystals at temperatures in the neighborhood of 77°K and below. With a stimulated crystal it was possible to induce the emission with an electric field of relatively low-field strength, ~10 V/cm; however, an unstimulated crystal could not generally be excited to emission at relatively high-field strengths (2–3 kV/cm). The Ag-In electrode arrangement (described above) was used and the emission occurred mostly in the neighborhood of the Ag electrode when it was biased in the positive direction. The emission was interpreted as recombination radiation arising from hole injection at the Ag electrode, even when an ac field was applied ("forming" seemed to play no role here). Smith[12] has previously observed electroluminescence in CdS at room temperature and 77°K; he reports "yellow spots" at the anode at low fields, which then change to "green spots" and finally to "green beams" across the crystal at higher fields. In similar experiments, Komiya *et al.*[13] have observed complicated luminescence "patterns" at room temperature. In our observations, only a continuous green emission appeared at the anode, i.e., no yellow or green spots were observed and the intensity appeared to increase with injection level.

In our previous experiments with the "tap" crystals, a rather curious and imperfectly understood anomaly in the conductivity was reported.[19] At 4.2°K, a sudden onset of extremely high conductivity was observed in optically stimulated samples. This occurred as the applied field was increased to a point (for some samples <100 V/cm) where the recombination radiation was of sufficient intensity to permit rapid spectral recording. The high crystal currents resulted in destruction of the electrodes and rapid boil-off of the liquid He. To prevent this, an electronic current limiter was used in the circuit, but the operating range of currents was still rather high (300–500 mA). Although it now appears that the previously reported spectral characteristics[19] were obtained at currents considerably above the negative resistance region (beyond the voltage minimum), green emission was still observable at currents well below the onset of high conductivity and undoubtedly arose from recombination of injected carriers. Lampert's semiinsulator, double-injection model[1] lead us to suspect that the high conductivity in the "tap" crystals might have been due, at least at 4.2°K, to a negative resistance "regime."

B. Current-Voltage Characteristics

We have recently investigated the current-voltage characteristics of several CdS "tap" crystals at both 77 and 4.2°K. As shown in Fig. 1, a log-log plot of current-voltage for a "tap" crystal at 77°K does reveal a negative resistance characteristic similar to that predicted by Lampert's model. At low currents, the current appears to be largely space-charge limited (single-carrier injection) and follows an approximate V^2 dependence.[23] As

[23] The V^2 dependence is not restrictive but mainly rests on several assumptions, not the least of which is the assumption of nontrapping of injected carriers. M. A. Lampert and A. Rose [Phys. Rev. **121**, 26 (1961)], have discussed the assumptions that may not be realized under actual experimental conditions.

the voltage and current increase, however, a threshold voltage, V_t, for double-carrier injection (injection from "good" contacts, in case Lampert's model applies) is reached at approximately 16 V ($I=0.5$ mA) after which the slope of the curve changes sign, marking the onset of the negative resistance and semiconductor regions. In qualitative agreement with Lampert's theory, the voltage decreases with increasing current through the negative resistance region to a minimum, $V_m(\sim 13$ V), after which it starts to rise again. The theory predicts that a current increase, following V_m, should first follow a V^2 dependence and then a V^3 dependence, with the current in the V^2 region being largely recombination limited and in the V^3 region both recombination and space-charge limited. In Fig. 1, the rise of current and voltage after V_m appears to be ohmic rather than power law, but little significance can be attached to this since the crystal was saturated.

On the basis of Lampert's model,[1] the hole and electron-trapping cross sections, as well as the high and low injection-level hole lifetimes, are related by

$$\frac{V_t}{V_m}\approx\frac{\sigma_p}{\sigma_n}\approx\frac{\tau_{\text{high}}}{\tau_{\text{low}}}. \tag{1}$$

Assuming that Lampert's model applies, one finds (Fig. 1) that $\sigma_p/\sigma_n\approx\tau_{\text{high}}/\tau_{\text{low}}\approx 1.3$ for the given crystal at 77°K. Of course, in Lampert's model, V_t/V_m and, in turn, σ_p/σ_n and $\tau_{\text{high}}/\tau_{\text{low}}$ are dependent on injection level (electric field strength), while in our results, V_t/V_m also depends on the initial level of optical stimulation. It appears that the "tap" crystals do not display a true negative resistance at 77°K, even though the I-V characteristics seem to follow the general features of both the Lampert[1] and SAL[10] models.

It should be pointed out that the current-voltage characteristic of a "tap" crystal is irreversible at 77°K and, in general, the same I-V curve cannot be retraced for a given level of stimulation. Apparently, the crystals "pump themselves up," as it were, to a higher level of stimulation by absorption of their own recombination radiation. This reasoning is supported by the observation that the current slowly increases in an optically stimulated crystal, provided the applied potential is high enough to induce emission, even when the crystal is in a totally darkened room. On the other hand, the I-V characteristic of a crystal at 4.2°K is completely reversible and can be retraced at will by simply reducing the bias voltage to zero and then increasing it again, provided that the maximum current reached in the negative resistance region is not too high. When the current rises too far into the negative resistance region (beyond V_m) there is a quenching of the optical stimulation and double injection, due possibly to ohmic heating, after which it is necessary to optically restimulate the crystal before the curve can be retraced at the same bias voltage.

Figure 2 shows an I-V oscilloscope trace (linear plot)

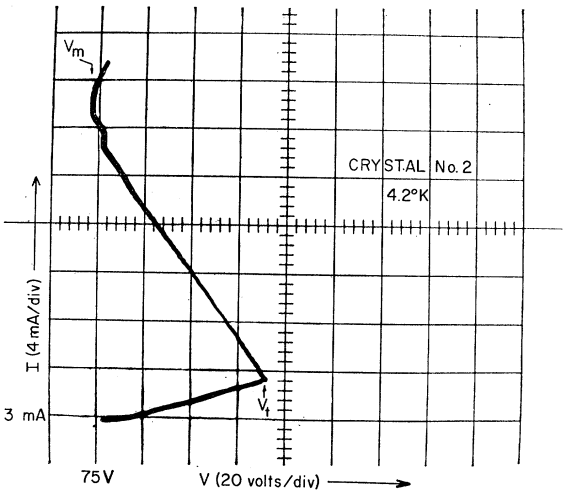

FIG. 2. Oscillograph of the current-voltage characteristic of CdS "tap" crystal No. 2 at 4.2°K. The values of V_t and V_m are, respectively, 145 V ($I=7$ mA) and 75 V ($I=29$ mA).

for a "tap" crystal at 4.2°K, and here one observes a pronounced negative-resistance characteristic. The voltage increases with current through what is usually a space-charge-limited region (here nearly a linear variation[23] of I with V) to V_t, after which double carrier injection becomes operative and the voltage drops very sharply into the negative-resistance region as the current increases. As the current continues to increase, a voltage minimum V_m is finally reached, after which the voltage begins to rise again with increasing current. Again assuming that Lampert's theory holds, one finds for the given crystal, field strength, and stimulation (Fig. 2) that $V_t/V_m\approx\sigma_p/\sigma_n\approx 1.9$. A negative-resistance characteristic was observed in all the tap crystals we investigated at 4.2°K; for a given crystal, V_t/V_m was always greater at 4.2 than at 77°K.

Since the "tap" crystals showed a definite negative-resistance characteristic at 4.2°K, it was felt that the crystals could be driven to oscillation when biased in the forward direction into the negative-resistance region. Crystal No. 2 (Fig. 2), in series with a 28-V wet-cell supply, was connected to an RLC tank circuit. The crystal was optically stimulated and the bias voltage was increased until the current was at or near the threshold voltage, V_t. At this point it was possible to set the crystal into reasonably stable oscillation by tuning the tank circuit. The oscillations were detected with an oscilloscope connected across the tank circuit capacitor. The waveform was rather complicated and we did not determine the frequency of the oscillation; however, there was some evidence of multiple frequencies and damping in the oscillation.

C. Interpretation of Negative Resistance

Given in Fig. 3 is an energy model, previously proposed for mechanically excited emission in CdS,[18,19] in

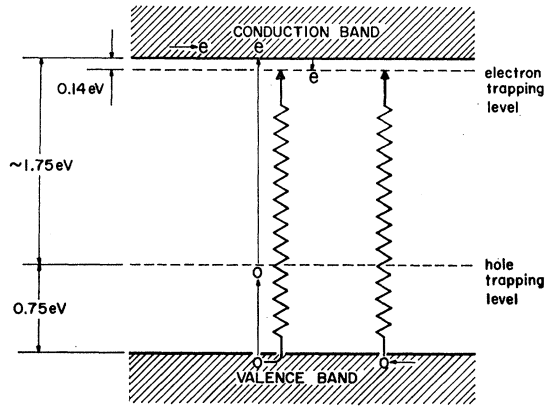

FIG. 3. Energy model for edge emission and double injection in CdS "tap" crystals. The wavy arrows represent radiative transitions and the solid arrows those of stimulating absorption and thermalization. A mirror reflection of the given trapping levels about the center of the forbidden gap would serve equivalently in the interpretation of recombination and injection.

terms of which the double-carrier injection and field-induced emission may be interpreted. In this model, the crystal is stimulated by absorption of radiation whose photon energy is at least as energetic as 1.75 eV.[20] This absorption excites electrons to the conduction band, some of which thermalize to the electron-trapping level[24]; the holes created at the hole-trapping level (0.75 eV above the valence band[20]) remain trapped at this level, for reasons we are not yet able to explain.[25] Now the holes will remain trapped as long as the crystal is in a stimulated condition. This condition will prevail until the crystal is either mechanically excited to emission, or exposed to infrared radiation at least as energetic as 0.75 eV.[20] The infrared radiation destimulates the crystal by exciting the trapped hole to the valence band where it recombines with a trapped electron in a radiative transition.

Negative resistance and field-induced emission are not observed in these crystals until they are placed in a stimulated state by irradiation with light of at least 1.75-eV photon energy. If a given crystal is cooled to 4.2°K in the dark and is not subsequently stimulated, electric fields up to the breakdown voltage of the crystal can be applied without observing either negative resistance or emission. (In most unstimulated crystals, fields as great as 3 kV/cm would not produce breakdown effects or negative resistance.) After stimulation, however, the conductivity of the crystals is appreciably increased,[18,19] at which time negative resistance and field-induced emission are observed at very low applied voltages. In some crystals, where the electrode spacings were small (~1 mm), the onset of negative resistance was observed at applied voltages ~5 V. Here, as usual, the crystals were biased such that the Ag electrode was the anode. One has to be careful in the stimulation process, however, as it is possible to saturate the crystals with the 1.75 eV photons. Once a partially-stimulated crystal is overstimulated (saturated), it is impossible to obtain negative resistance at any temperature. Apparently, in this case, the "blocking characteristic" of an initially good diode is removed and the crystal is driven completely into a semiconductor "regime," a fact which has been previously observed in Ge by Holonyak *et al.*[4]; moreover, it has been pointed out[4] that such semiconduction is probably due to trapping levels not accounted for in Lampert's theory.[1] In Fig. 2, V_m is the threshold voltage for a given level of optical stimulation (short of saturation). For higher initial levels of stimulation (not shown in the data), V_m occurs at lower voltages. Finally, at saturation, $V_m \sim V_t$, and the negative characteristic disappears.

When a crystal is optically stimulated, we propose that two effects will occur:

(1) The steady-state hole Fermi level (SSHFL) will, in order to adjust to the new charge distribution (consequence of trapping), move to a position which appears more favorable for hole injection at the Ag electrode.

(2) Many of the hole traps in the crystal will be filled so that the lifetimes of the injected holes will be appreciably increased (model, Fig. 3).

These two effects should make it possible to observe a pronounced and stable negative resistance in the "tap" crystals. The accompanying emission is a consequence of the recombination of injected carriers, preferentially in this case, at the edge-emission recombination center.

The conditions necessary to observe the negative resistance reported here, as well as the onset of negative resistance, differ from the conditions under which negative resistance has previously been reported in CdS.[12,13] In our results, e.g., the stable and reproducible negative-resistance characteristic occurs only in a stimulated crystal near 4.2°K; moreover, the electric field required for the onset of negative resistance is at least an order of magnitude lower than that reported by Smith.[12] On the basis of voltage probe measurements (cathode to anode), Smith established that anode breakdown was a necessary condition for double injection in the crystals he examined. There are several reasons which indicate that contact breakdown is not likely in our results:

(1) The negative resistance occurs at very low-field strengths.

(2) Negative resistance does not occur at 77°K in the same crystal that exhibits negative resistance at 4.2°K,

[24] This trapping level is due to the green, edge-emission center and is located approximately 0.14 eV from a band edge; B. A. Kulp and R. H. Kelley, J. Appl. Phys. **31**, 1057 (1960), have shown that the edge emission center is due to the sulfur interstitial atom.

[25] Our present thinking on the mechanism of mechanically excited emission is that the trapped carriers (holes in the present argument) are released either by a moving dislocation (set in motion by the mechanical tap), or by a short-lived piezoelectric potential (since CdS has a very high piezoelectric constant), generated by the mechanically induced shock wave and moving through the crystal in the form of a dipole field. Neither hypothesis has been experimentally established.

even when it is stimulated to the same resistance and the same voltage is applied. One would expect that, under the conditions of contact breakdown, such breakdown would occur at both temperatures.

(3) The diode blocking characteristic (forward to backward ratios often as great as several orders of magnitude in a partially stimulated crystal) could be completely removed from a crystal by complete stimulation (saturation) with light, presumably driving the crystal completely into the semiconductor region.[1,4]

In the CdS "tap" crystals, we propose that the negative-resistance results from double-carrier injection: electron injection at the In electrode and hole injection at the Ag electrode. In terms of the model (Fig. 3) one can reason that, initially, the lifetime of the holes is increased by filling the hole traps (absorption of stimulating radiation). The hole lifetime is further increased with higher injection levels, resulting in negative resistance in basic agreement with Lampert's theory.[1] We also propose that the lifetimes of the free carriers (both holes and electrons) vary with injection level, a basic assumption on which the theory rests and a point which is difficult to quantitatively demonstrate in our results. In Lampert's theory, the condition that leads to a marked negative resistance is $\sigma_p \gg \sigma_n$, where σ_p and σ_n are the trapping cross sections for free holes and electrons, respectively. This condition does not hold strongly in our case, since, e.g., $\sigma_p \approx 2\sigma_n$ (data of Fig. 2). Perhaps this is due to a changing cross section for the electron-trapping level in our model (Fig. 3), where trapped electrons are lost to recombination radiation and replenished by optical self-stimulation, via thermalization from the conduction band.

In the SAL theory[10] for current-controlled, contact breakdown-induced negative resistance in semiconductors, free-carrier lifetimes are essentially constant with increasing injection level. In a test of this theory, using data[10] for p- and n-type Ge diodes, they find good agreement between measured and calculated current densities, voltage drops, negative resistance and current oscillations. It is difficult to test our data (even semi-quantitatively) in terms of this theory since good free-carrier mobility and lifetime data are not available for the CdS "tap" crystals (Hall mobility measurements are difficult at 4.2°K, particularly in stimulated "tap" crystals, as there is a constant drift in the Hall voltage, even at low crystal voltages). There is, however, some evidence that the carrier mobility of the "tap" crystals increases with increasing injection level[26] (Hall measurements) but no lifetime data is available.

In the SAL theory,[10] the criterion that must be satisfied in order to obtain negative resistance in n-type material is

$$E_A\left(\frac{D_2^2}{D_1^2}\right)\frac{\mu_p\tau}{L_1} > 1, \tag{2}$$

where E_A is the threshold voltage for double injection, D_2 and D_1 are, respectively, the anode and cathode contact diameters ($D_1 > D_2$ and neither contact is a source of minority carriers before contact breakdown), L_1 is the sample length ($L_1 \gg D_1$), and $\mu_p\tau$ is the mobility-lifetime product for injected holes. Assuming that normal, room temperature CdS data applies, one can compute the above expression for our results. From the data of Fig. 2, one finds that $E_A \approx 145$ V; $D_2^2/D_1^2 \approx 0.25$ and $L_1 = 1$ cm. Using a room temperature $\mu_p\tau$ value of 5.4×10^{-6} cm^2/V ($\mu_p = 18$ cm^2/Vsec and $\tau = 3\times10^{-7}$ sec), due to Mort and Spear,[27] one obtains for (2) a value $\sim 2\times10^{-4}$. Hence, one finds that $E_A(D_2^2/D_1^2)(\mu_p\tau/L_1) \ll 1$, in apparent violation of the breakdown-induced injection criterion, assuming that the room temperature $\mu_p\tau$ holds at 4.2°K. Actually, $\mu_p\tau$ would have to increase by more than four orders of magnitude in order to reverse the inequality of (2) for our data; also, the condition $L_1 \gg D_1$ does not hold in our results.

Perhaps it is well to emphasize that both the Lampert[1] and SAL[10] theories lead to a prediction of negative resistance, the essential difference being the mechanism by which the carriers are injected into the bulk: Lampert's theory assumes double injection into the bulk from "good" injecting contacts, while the SAL theory assumes bulk injection from breakdown of at least one of the contacts. In general, our results are more nearly in keeping with Lampert's model, but our data does not provide direct evidence as to how the carriers are injected into the bulk.

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[26] R. G. Schulze (private communication).

[27] J. Mort and W. E. Spear, Phys. Rev. Letters 8, 314 (1962). See also D. L. Mills, W. J. Price, D. C. Reynolds, and W. L. Lehmann, Bull. Am. Phys. Soc. 7, 542 (1962).