COHERENT MICROWAVE RADIATION FROM BiSb ALLOYS

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Microwave radiation is observed from electrically biased semiconducting BiSb alloys. The radiation emitted from $Bi_{92}Sb_8$ and its harmonics to the fourth order are very narrow band and coherent. The mechanism of emission is postulated to be a super-radiant maser effect due to transitions between paramagneticlike levels pumped by the electric current.

Microwave radiation of largely unexplained origin has been observed from InSb [1,2] and InAs[3] semiconductors under various conditions of applied magnetic and electrical fields at cryogenic temperatures. BiSb alloys were studied in an attempt to increase the understanding of this process.

While the details of the band structure of $Bi_{1-x}Sb_x$ are still being debated,[4] it is generally agreed[5] that for antimony concentrations of $x \leq 0.06 \pm 0.01$ the alloys are semimetallic with overlapping conduction and valence bands. Above $x = 0.06$ the system becomes a semiconductor with a very small energy gap which increases with increasing (up to about $x = 0.15$) Sb concentrations. We have examined a number of these alloys (from $x = 0.00$ to 0.16) for emission of microwave radiation when the samples were cooled to cryogenic temperatures and subjected to biasing electrical and magnetic fields. In this Letter we report the observation of microwave radiation from weakly biased (0.9 V/cm $< E < 15$ V/cm) $Bi_{92}Sb_8$ alloys,[6] discuss its properties, and propose a mechanism that accounts for our observations.

The samples, with typical dimensions of $1 \times 1 \times 10$ mm^3, were cut from boat-grown BiSb alloys prepared from 99.9999% pure Bi and Sb. Gold wires were soldered to the ends of the samples with a variety of low melting point solders. The samples were then placed near the end of a nonresonant coaxial transmission line immersed in a cryogenic fluid. The transmission line was connected either to a sensitive radiometer or to a rf spectrum analyzer. Microsecond current pulses were applied to the low-impedance samples by means of a strip line.

The radiation from the $Bi_{92}Sb_8$ alloy was the most interesting. An example of the electric-field–frequency dependence of this radiation is shown in Fig. 1. The radiation is observed only along the loci[7] shown and consists of three families $n = 1, 2, 3$ and their harmonics $l = 1, 2, 3, 4$. In subsequent discussion the branches will be referred to by the numbers associated with the letters $(n; l)$. A number of 8%-Sb samples showed this basic emission pattern, the dominant feature being two fundamental curves (1; 1), (2; 1) with apex (minimum) frequencies near 700 and 1000 MHz. These two frequencies therefore appear to be a characteristic of the emission from the 8% samples.

Changing the temperature from 4.2 to 1.8°K had no effect on the apex frequencies; however, there was a shift to a more symmetrical curve at 1.8°K in the upper branch of the family $n = 2$ as is shown in (2; 1). The radiation was observed also at 20.4°K (but not at 64°K) with the same basic properties, so that temperature does not seem to be a significant variable except in quenching the effect.

External magnetic fields, both perpendicular and parallel to the current, were found to shift the curves in a complicated and sensitive way. In some orientations df/dB reached about 5 MHz/G. External fields of 50 to 100 G were usually sufficient to quench the radiation completely. The dependence of emission frequency on the external magnetic field led us to conclude that the frequency of emission was being tuned by the self magnetic field of the applied current (pulses of up to ~70 A produced self fields up to ~280 G at the sample surface).

A peak emitted microwave power of about 20 μW was observed near the apex of the curve (2; 1). The emitted power in all curves was a maximum near the apex and decreased rapidly at higher frequencies in both the upper and lower branches, as illustrated for the lower branch of (2; 3) by the curve at the bottom of Fig. 1. The power decreases in successive harmonics at about 3 to 10 dB per harmonic. Microwave emis-

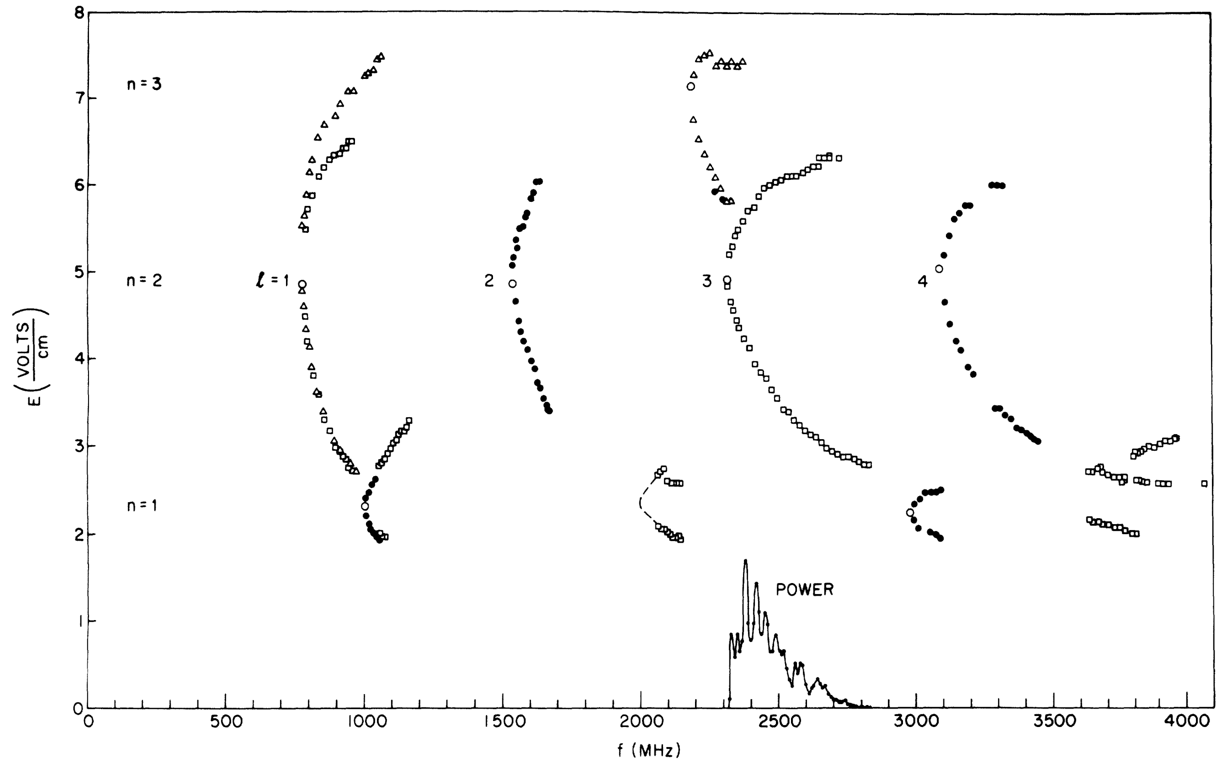

FIG. 1. Frequency of emitted radiation as a function of electric field in a sample of $Bi_{92}Sb_8$. The carrier concentration and mobility at 4.2°K in this sample are 2.3×10^{16} electrons/cm^3 and 300 000 cm^2/V sec. Solid dots: data at 4.2°K before event described in Ref. 7; open squares: data at 4.2°K after the event. Open triangles were taken at 1.8°K after the event, and open circles denote points of minimum observed frequency. The curve labeled "power" shows in arbitrary units the power emitted in the lower branch of curve $n=2$, $l=3$. In this case there is a residual external magnetic field of 2.9 G, which plays no significant role in the behavior. The current pulse length is 3.7 μsec and the pulse repetition rate is ~40 Hz.

sion was sought but not observed in the range 4 to 44 GHz.

The harmonic relationships between the curves are valid within the experimental accuracy (~1 %), except for the segments of (1; 4) near 4000 MHz which are probably an i.f. image of the fourth harmonic. If the microwave generation region is as small (~10 μ) as believed, then the resulting high microwave power density (~1-10 kW/cm^3) would be favorable for nonlinear processes. Therefore the harmonics are thought to arise as the result of electronic nonlinear harmonic generation and mixing.

The frequency and power of the emitted radiation are largely independent of the length of the samples which tends to rule out a Gunn-like effect. On the other hand the curves are sensitive to the electric field polarity although I-V characteristics are reciprocal and Ohmic, which suggest an effect at or near the contacts. The contacts for this sample were a BiPbSn (Au-doped) alloy.

The most significant property of the radiation is its narrow-band, coherent nature. For example, when the radiation was observed at the apex of (2; 1), a long (2.5 μsec) burst of rf was obtained and its bandwidth was measured to be 0.1 ± 0.03 MHz. This bandwidth is within a factor of 2 of the theoretical minimum obtainable for a burst of this length due to a finite-length wave packet. At frequencies away from the apex only short (~250 μsec) rf bursts are observed because the current pulse is not quite flat and, unlike at the apex, the frequency tunes rapidly (see Fig. 1) with field. In this case the bandwidth of the radiation is proportionally larger, that is about 1.5 MHz.

The extremely narrow bandwidth radiation is an intrinsic property of BiSb since the coaxial transmission line is not resonant and the sample is much too lossy to form a high-Q cavity. The coherence and very narrow bandwidth suggest that the emission is caused by a special type of bulk instability in the electron plasma or by an atomic maser process. Neither BiSb nor InSb narrow-band emission is satisfactorily explained by known bulk instabilities. Here we postulate that the $Bi_{92}Sb_8$ radiation is due to a dc-pumped, super-radiant maser process between paramagnetic spinlike levels located in the BiSb at or near the contacts. We also point out that the InSb radiation[8] periodicity in B also indicates an energy level scheme.

Magnetically determined spin level splittings of a form which would account for the data of Fig. 1 are well known from paramagnetic resonance studies; for example, the magnetic field dependence of the paramagnetic levels of Cr^{3+} in ruby which are shown in Fig. 2(a). Considering transitions between the spin energy levels 2 and 3, it is apparent that at some frequency f_1 ($>f_0$) there will be two magnetic field values at which microwave energy may be absorbed or emitted between levels 2 and 3. As the frequency is lowered the two field values move closer together until the minimum splitting f_0 is reached, below which frequency no more energy will be absorbed or emitted between levels 2 and 3. This is a description of the frequency dependence of the microwave emission of Fig. 1, provided one changes the vertical axis to read self magnetic field of the current instead of electric field. Figure 2(c) illustrates the energy difference for curve (2; 1) (assuming a transition between energy levels) as a function of maximum self magnetic field.[9]

The principal argument that this is a maser process is based on the bandwidth properties discussed above. If this were due to spontaneous emission, the bandwidth (at the apex) of 0.1 MHz would require a lifetime of ~3 μsec and the radiation would decay to $1/e$ in a time of this order, as already shown by Feher et al.[10] for paramagnetic spontaneous emission in Si. However, the BiSb stops emitting completely in a time ~200 μsec after the current pulse is turned off. Furthermore, the narrow (250 μsec) rf pulses slightly away from the apex should have approximately the same relaxation time as at the apex, but their decay is nearly two orders of magnitude faster than suggested by the spontaneous emission relaxation time of ~3 μsec.

We list below some other similarities of the present observations to paramagnetic states and masers: (1) BiSb emits only at cryogenic temperatures, a common property of conventional microwave masers. (2) The tuning due to external and internal magnetic fields is within a factor of 2 of that for electrons with a g factor of 2,[11] i.e., 2.8 MHz/G. (3) There are various conditions which make the radiation appear and disappear discontinuously similar to a threshold

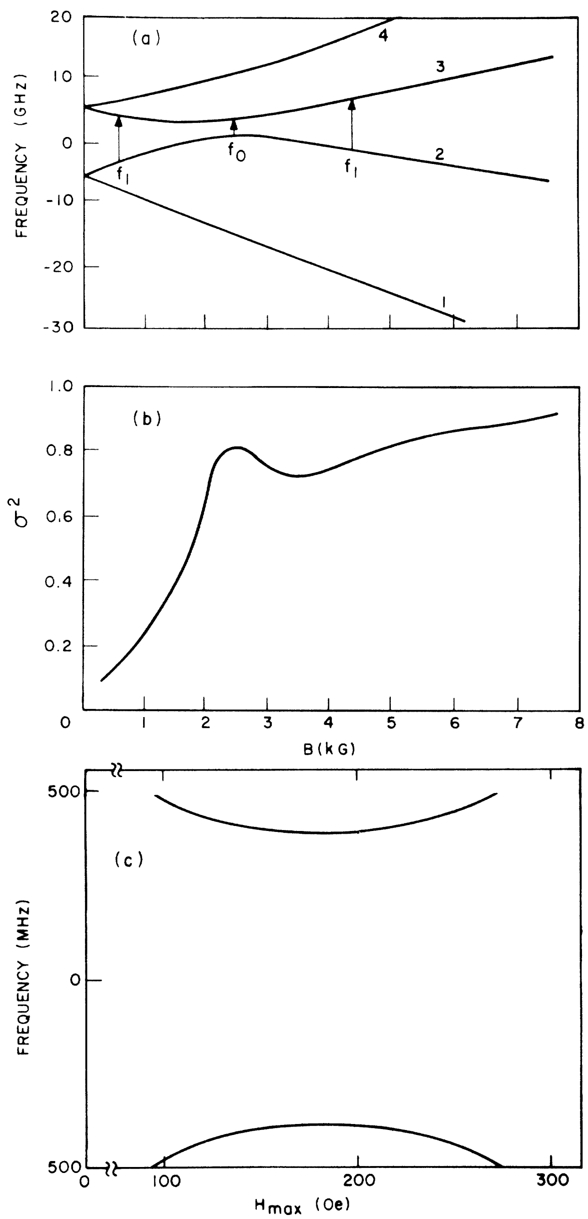

FIG. 2. (a) The energy-level diagram of ruby as a function of magnetic field for an angle of 30° between the optical axis and the magnetic field. The arrows indicate possible transitions between the levels at frequencies f_1 and f_0. (b) Maximum values of the transition-probability matrix elements as a function of magnetic field in ruby for the case shown in (a) above. (c) The energy-level diagram at 1.8°K represented by curve (2; 1) in Fig. 1 as a function of maximum (surface) self magnetic field.

effect in a maser. (4) The transition-probability matrix elements calculated[12] for ruby [see Fig. 2(b)] show an increase near the minimum energy separation, as does the emitted power upon approaching the minimum frequency in the present case (Fig. 1).

Neither the precise nature of the states nor the mechanism pumping them has been established. One possible pumping mechanism is that noted by Clark and Feher[13] in studies of the effect of drift current on nuclear magnetic resonance in InSb. In their experiments the sign of the g factors in the contact material and in the InSb semiconductor ($g_{InSb} = -56$) are opposite, which means that those electrons which are injected from the contact into the InSb and do not undergo a spin-flip transition will find themselves at a negative spin temperature. They found evidence of a negative polarization (but not necessarily negative temperatures) in the neighborhood of the negatively biased contact. This mechanism, while unproved in the present case, is in agreement with the observation that the contacts play an important role and that the radiation is probably emitted at or near the contacts.

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[6]Radiation has been observed also from $Bi_{95}Sb_5$ and $Bi_{88}Sb_{12}$ alloys and will be reported in a later publication.

[7]At one time this sample was accidentally overheated, which changed slightly the electric field values, but not the overall pattern of the radiation. The solid points of Fig. 1 were taken before this event and have been arbitrarily shifted down in electric field by 8% to facilitate presentation of the data.

[8]G. Bekefi, A. Bers, and S. R. J. Brueck, IEEE Trans. Electron Devices 14, 593 (1967).

[9]The emission is believed to originate from a small region within a skin depth (50 μ). Therefore the magnetic field in this region is within 10% of the maximum self magnetic field.

[10]G. Feher et al., Phys. Rev. 109, 221 (1958).

[11]Such a small g factor would contraindicate the BiSb conduction electrons for which $|g| \approx 100$.

[12]See for example, A. E. Siegman, Microwave Solid State Masers (McGraw-Hill Book Company, Inc., New York, 1964).

[13]W. G. Clark and G. Feher, Phys. Rev. Letters 10, 134 (1963).

SIMPLE BAND MODEL FOR AMORPHOUS SEMICONDUCTING ALLOYS*

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Because of the near perfect local satisfaction of the valence requirements of each atom, which is complemented by the positional and compositional disorder, covalently bonded amorphous alloys are intrinsic semiconductors. We describe a band model with some novel features, which successfully describes several important effects observed in these amorphous semiconducting alloys.

Amorphous covalent alloys particularly of group-IV, -V, and -VI elements are readily formed over broad ranges of composition.[1-6] They have been described as low-mobility electronic intrinsic semiconductors with a temperature-activated electrical conductivity $\sigma = \sigma_0 \times \exp(-\Delta E/kT)$ which sometimes extends well into the molten state.[2,3,7] They remain intrinsic