Letters to the Editor

PUBLICATION of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is five weeks prior to the date of issue. No proof will be sent to the authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not exceed 600 words in length and should be submitted in duplicate.

Direct Transition Exciton and Fine Structure of the Magneto-Absorption Spectrum in Germanium*

SOLOMON ZWERDLING,† LAURA M. ROTH,† AND BENJAMIN LAX†
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts
(Received January 23, 1958)

WE have observed exciton[1] absorption just below the direct gap in germanium, together with the fine structure of the related oscillatory magneto-absorption.[2] The exciton was also studied at various magnetic fields. The measurements were made at 4.2°K on an $\sim$4-μ sample with **B** along a [100] axis and the surface. A double-pass monochromator with a 15 000-line/in. grating and a PbS detector provided resolution between 10–20 000. Figure 1 shows the magneto-absorption spectrum for $\mathbf{E}\|\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$ to 1.01 ev (oscillations were observed to 1.07 ev).

An analysis of the Landau spectrum[3] was made using the Luttinger-Kohn model for the valence band levels with selection rules $\Delta n=0$, -2 for transitions between the two sets of heavy- and light-hole levels and the $k=0$ conduction band levels, with n the magnetic quantum number. Additional selection rules for m_j (valence band) and m_s (conduction band) are $\Delta m=0$ for $\mathbf{E}\|\mathbf{B}$, and $\Delta m=\pm1$ for $\mathbf{E}\perp\mathbf{B}$. A preliminary identification of some of the lines shown in Fig. 1 was obtained by correlation with a theoretical tabulation of energy *versus* n. The transitions between light-hole and electron levels gave good agreement, and those involving heavy-hole levels were consistent although the $\Delta n=0$, -2 transitions were not resolved. Using pairs of lines 6′ and 10, and 11 and 14′, correcting for the spin splitting of the electron levels and the decreasing curvature of the conduction band, the electron mass at the band minimum was found to be $m_c^*=(0.035\pm0.001)m_0$. The spin splitting from lines 7′ and 7 corresponds to a g factor[4] of -3. The conduction-band Landau levels near $k=0$ are closely given by $E_n=3.27\times10^{-4}(n+\frac{1}{2})B-1.42\times10^{-7}(n+\frac{1}{2})^2B^2$, with B in kilogauss and E_n in ev. Detailed analysis of these results and those for the valence band will be published later.

Since lines 1, 1′, and 3 apparently did not fit the theoretical spectrum for transitions between Landau levels, their magnetic dependence was studied as shown for 1′ in Fig. 2. Since line 1′ appears strongly at zero field, we conclude that it is associated with the transition to the lowest exciton level below the direct gap. Further

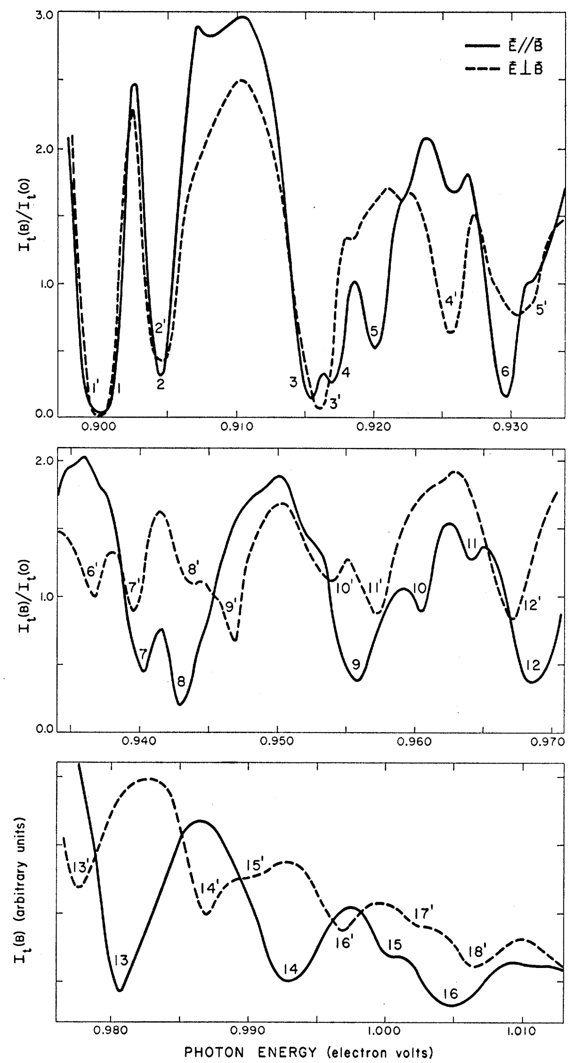

FIG. 1. Fine structure of oscillatory magneto-absorption spectra for 38.9 kilogauss. Prominent minima fall into sequences representing transitions from the four sets of valence band levels $\epsilon(\bar{n},1\pm)$, $\epsilon(\bar{n},2\pm)$ [following the notation of J. M. Luttinger, Phys. Rev. **102**, 1030 (1956)] to the two sets of conduction band levels $n\alpha$ (spin up) and $n\beta$ (spin down). Here n and $\bar{n}$ are quantum numbers for the magnetic levels, and $+$ and $-$ refer to light- and heavy-hole levels respectively. In the following, for example, $\epsilon(n+2,1+)\rightarrow n\alpha$ represents transitions from the first set of light-hole levels to the spin-up electron levels, with the selection rule $\Delta n=n-\bar{n}=-2$. (a) $\mathbf{E}\perp\mathbf{B}$. Light hole: $\epsilon(n+2,1+)\rightarrow n\alpha$, $n=0$—4 (lines 3′*, 6′, 11′, 13′*, 16′); $\epsilon(n,2+)\rightarrow n\beta$, $n=0$—5 (lines 2′*, 4′, 9′, 12′*, 14′, 18′); $\epsilon(2,1+)\rightarrow2\alpha$ (line 7′). Heavy hole: $\epsilon(n+2,1-)\rightarrow n\alpha$, $\epsilon(n+2,2-)\rightarrow n\beta$, $\epsilon(n,1-)\rightarrow n\alpha$ $(n\neq0,1)$, $\epsilon(n,2-)\rightarrow n\beta$ $(n\neq0,1)$, (unresolved), $n=0$—8 (lines 2′*, 3′*, 5′*, 8′, 10′, 12′*, 13′*, 15′, 17′). (b) $\mathbf{E}\|\mathbf{B}$. Light hole: $\epsilon(n,1+)\rightarrow n\beta$, $n=0$—5 (lines 2*, 5, 7, 10, 13*, 15); $\epsilon(4,2+)\rightarrow2\alpha$ (line 11). Heavy hole: $\epsilon(n,1-)\rightarrow n\beta$ $(n\neq0,1)$, $\epsilon(n+2,2-)\rightarrow n\alpha$, (unresolved), $n=0$—8 (lines 2*, 4?, 6, 8, 9, 12, 13*, 14, 16*). (The asterisk indicates overlapping in addition to unresolved heavy hole lines.)

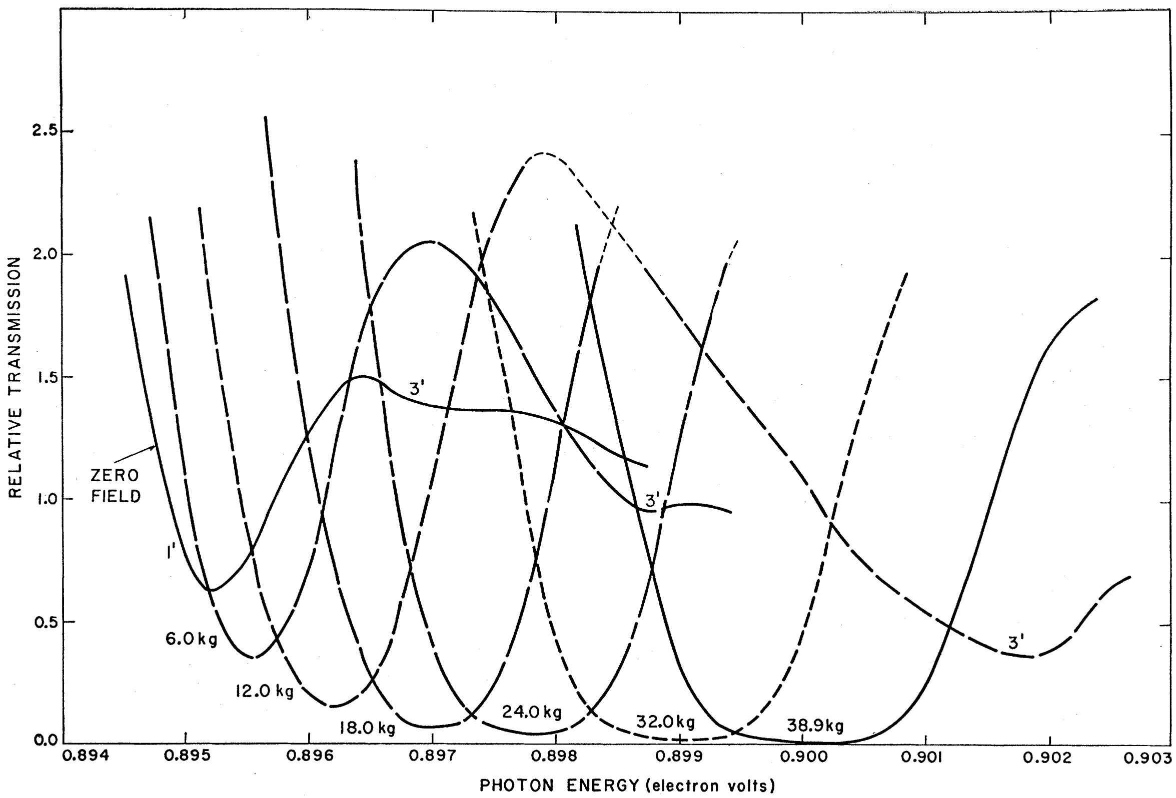

FIG. 2. Lowest exciton line at various magnetic fields for **E**⊥**B** (1′). Similar behavior was found for **E**‖**B** (line 1). Second exciton line (3′) is shown for the lower fields and at 12 kilogauss overlaps first Landau transition.

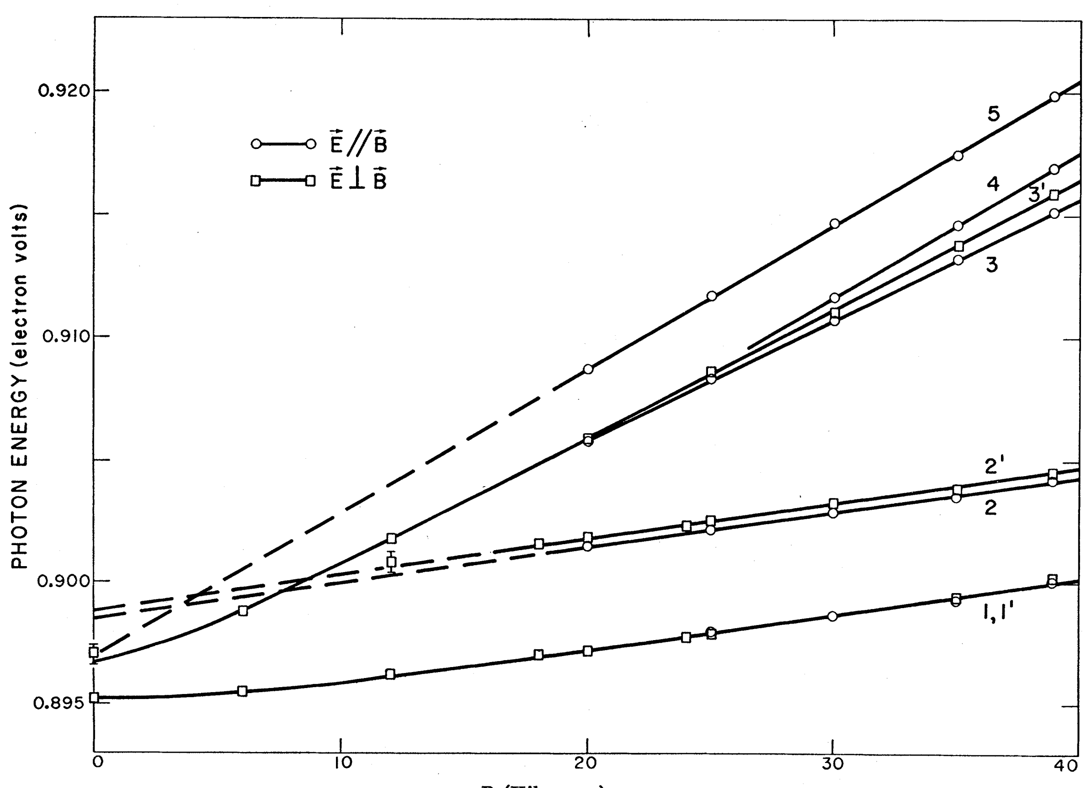

FIG. 3. Position of exciton and two lowest Landau transitions as a function of magnetic field.

evidence is provided in Fig. 3. Lines 2, 2′, and 5 are identifiable as Landau lines, and their intensities drop sharply with decreasing field, as expected theoretically.[3] Their mean extrapolated value of 0.898 ± 0.001 ev is the 4.2°K direct gap. Line 1′ appears nonlinear at lower fields, as expected for a hydrogen-like s level in a large magnetic field.[4] The experimental binding energy of the lowest exciton level is ~ 0.0025 ev as compared with the theoretical estimate of 0.0017 ev, obtained[1] from $E_N^{\mathrm{ex}} \cong 13.60\mu^*/K^2N^2m_0$, using $\mu^* = 0.031m_0$ as a reduced mass, $K = 16$ as the dielectric constant, and N as the exciton quantum number. The uncertainty in the gap and possibly in K, and an expected shift of the Landau lines due to scattering may account for the discrepancy. For such large orbits ($r \cong 500a_0$), estimates from effective mass theory should be reliable. At 38.9 kilogauss, the binding energy is found to be 0.0043 ev, as compared to 0.0045 ev calculated from the results of YKA.[4]

Evidence for the next higher exciton state, lines 3′ and 3 (and 4?) is shown in Fig. 3. A polarization effect occurs with a possible splitting in the parallel case. Fine structure should also appear in the first exciton line, due to the degenerate valence band. The broadening at high fields is probably due to such unresolved structure. Lower temperature, higher fields, thinner samples, and annealing are indicated. The latter is suggested from the line width which gives $\tau \approx 4 \times 10^{-12}$ sec at 4°K, smaller than that from cyclotron resonance.

We are grateful to Mr. J. P. Theriault for assisting with the experiments, to Dr. D. H. Dickey for the difficult task of reconstructing the cryostat for use in these measurements, to Mr. A. D. Jones for preparing the samples, and to Mrs. Jane S. Coe for reducing the data.

* The research reported in this document was supported jointly by the U. S. Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

† Staff members, Lincoln Laboratory, Massachusetts Institute of Technology.

[1] The theory of excitons in germanium has been treated by G. Dresselhaus, J. Phys. Chem. Solids **1**, 14 (1956), and R. J. Elliot, Phys. Rev. **108**, 1384 (1957). Experimental evidence of excitons for the indirect transition has been obtained by Macfarlane, McLean, Quarrington, and Roberts, Phys. Rev. **108**, 1377 (1957).

[2] S. Zwerdling and B. Lax, Phys. Rev. **106**, 51 (1957); Zwerdling, Lax, and Roth, Phys. Rev. **108**, 1402 (1957).

[3] Roth, Lax, and Zwerdling (to be published).

[4] Yafet, Keyes, and Adams, J. Phys. Chem. Solids **1**, 137 (1956); L. I. Schiff and H. Snyder, Phys. Rev. **55**, 59 (1939).

Electron Spin and Phonon Equilibrium in Masers*

N. Bloembergen

Harvard University, Cambridge, Massachusetts

(Received January 24, 1958)

TOWNES and co-workers have recently[1] presented experimental evidence indicating that the relaxation rates in paramagnetic salts at temperatures below 4.2°K are not determined by the interaction between the spins and the lattice vibrations, but between the latter and the helium bath. The authors claim that the normally observed relaxation time, e.g., in KCo(Cr)(CN)$_6$, is characteristic of energy transfer between the phonons and the bath, whereas the heat contact between the spin levels and the phonons is a thousand times better. It is the purpose of this Letter to point out that the successful operation of this salt in three-level steady-state masers[2] is incompatible with this assumption about the relaxation rates, regardless of the operating frequencies of the maser.

Let ν_{13} be the saturating frequency, and ν_{23} be the frequency of maser amplification. It has been clear[1] that if the frequency ν_{13} is close enough to either ν_{21} or ν_{23}, the hot phonon band around ν_{13} would overlap one of the other resonances and essentially equalize the populations of all three spin levels.

Consider now the case that the three frequencies are widely spaced and no overlapping of phonon bands occurs. The spin populations of levels 2 and 3 are inverted corresponding to a negative spin temperature and maser action at the frequency ν_{23}. Suppose, however, that the contact with the phonons is good. Then a phonon band around ν_{23} will be heated up. Since the energy levels of a lattice oscillator have no upper bound, the phonon temperature will always remain positive. On the other hand, the spin temperature should be very close to this phonon temperature, because its heat contact is supposed to be so much better than between the phonons around ν_{23} and the bath. The steady-state equilibrium situation would necessarily be one in which the phonon temperature at ν_{23} would be very high and positive and the spin temperature at ν_{23} very high and negative. This means however that the population of spin levels 2 and 3 would be almost equal; whereas for maser action a fairly large difference in population is necessary. It may therefore be concluded that the situation visualized by Townes *et al.* is excluded in paramagnetic salts which allow for successful steady-state maser operation.

The use of the concept "temperature" can be avoided entirely, although we believe it has heuristic value in spite of its lack of rigor in the present context. The problem of the three-level maser and phonon equilibria may be formulated rigorously in terms of six unknowns. The spin populations n_1, n_2, and n_3, and the average lattice oscillator excitation quantum numbers in the three phonon bands $\bar{n}_{\mathrm{ph}}(\nu_{23})$, $\bar{n}_{\mathrm{ph}}(\nu_{21})$, $\bar{n}_{\mathrm{ph}}(\nu_{13})$. Imposition of the steady-state conditions gives five linear equations relating to transport of quanta at the three frequencies. A sixth relation is that $n_1+n_2+n_3$ be equal to the number of paramagnetic ions. The algebraic solution of these six equations confirms the conclusion that n_3-n_2 is very small if the contact betweeen the spins and phonons is better than between phonons and the bath.

In this treatment phonon-phonon collisions have been ignored. They probably are important in practice,