possible binding sites.

From the determined threefold binding site at 1.25 ± 0.1 Å, the oxygen-tungsten chemisorption bond length is found to be 2.08 ± 0.07 Å, which is very close to the sum of covalent radii of oxygen and tungsten ($r_W + r_O = 2.12$ Å). The oxygen-tungsten bond length determined here is consistent with the trend observed for $c(2\times 2)$ and $p(2\times 2)$ oxygen chemisorption on nickel.[8,9] Given an experimentally measured[10] work function change of $\Delta\varphi = 0.7$ eV, we estimate the amount of charge transfer from tungsten to oxygen to be $q/e = 4.4\%$, where e is the electron charge.

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Very Shallow Trapping State in Doped Germanium

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Submillimeter photoconductivity in doped germanium has been studied with a lamellar grating spectrophotometer. The observed photoconductivity is ascribed to a shallow trapping state such as D^- or A^+. However, our spectral peak energies and shapes are quite different from those previously reported by Gershenzon, Gol'tsman, and Mel'nikov.

Submillimeter photoconductivity in doped-Ge and -Si crystals has been investigated by Gershenzon and co-workers[1,2] using backward-wave tubes (BWT). In the case of Ge, they observed photoconductive response peaks in the energy region of 1–2 meV depending on the kind of impurity used as dopant. They ascribed the responses to electrons (holes) bound to neutral donors (acceptors); that is, to D^- (A^+) states.

In the present experiment, we study the photoconductivities in Ge crystals doped with As, Sb, and Ga impurities using a Fourier transform spectrometer with a lamellar grating, and observe photoconductivity spectra having peaks near 3 meV and spreading widely from 1 to 7 meV. However, we do not observe any photoconductivity structure at the energy positions reported by Gershenzon, Gol'tsman, and Mel'nikov.[1] The observed photoconductivity is confirmed to be due to a trapping center and it is inferred that the D^- (A^+) state is also the most probable candidate for the center.

The spectrometer used was a Beckman LR-100 lamellar grating spectrophotometer designed to operate over the region 3–70 cm^{-1}. A combination of a low-pass filter and a cooled quartz filter was used to emphasize the required spectral range and to reduce the room-temperature background radiation above 250 cm^{-1}. The measured relative photoconductivity intensities were calibrated by measuring the spectral distribution of the light source (mercury vapor lamp) just at the front of the sample using a Unicam Golay-cell detector. The accuracy of the wavelength scale of the spectrometer was verified by measuring the absorption spectra of a hexa-iodobenzene (C_6I_6) powder disk. The Ge specimens for the measurements were cut and shaped into about $4\times 5\times \sim 0.5$ mm^3 pellets, mechanically polished, and CP-4 etched after being tapered to avoid in-

terference-fringe effects in the photoconductivity measurements.

Figure 1 shows the submillimeter photoconductive responses of several Ge crystals with different impurities. These spectra could be observed only at temperatures below 4.2 K. In the uppermost part of Fig. 1 [Ge(As)], the spectrum obtained in Ref. 1 is reproduced for comparison. Though the peak position in all the spectra is almost independent of the kind of impurity, the spectral shape depends strongly upon the impurity used as dopant. Furthermore, photoconductivity could not be observed from a high-purity sample (7×10^{11} cm^{-3} impurity concentration).

For the case of n-type Ge, the following two experimental results suggest that the observed photoconductive response must be due to a trapping center:

(1) An experiment was performed for the purpose of examining the effect of the background radiation on the submillimeter photoconductivity by placing a *Reststrahlen* powder filter (TlCl + TlI + NaF) or a Ge filter in front of the sample to reduce the radiation capable of ionizing the donors. The change of the photoconductive response was almost inversely proportional to the resistivity change of the specimen, implying that reduction of the conduction electrons results in a proportional reduction of the electrons trapped in the trapping center.

(2) The temperature dependence of the photoconductive response was measured on a sample containing 6.2×10^{14} cm^{-3} Sb. In this case, ultrasonically cut "bridge"-shaped specimens were employed for simultaneously measuring the resistivity and the Hall coefficient of the sample as a function of temperature.

Figure 2 shows the temperature dependence of the photoconductive response for the Ge(Sb) sample. In this figure, all the spectral photoresponses are normalized at 10 meV, assuming that the number of carriers excited from the 1s ground state to the conduction band is independent of temperature. By this normalization, we can ignore the temperature dependence of the carrier lifetime and mobility and can assume that the relative photoresponse at the peak near 3 meV is proportional to the number of carriers excited by the submillimeter radiation.

In this figure alone, the spectra are not calibrated for the spectral distribution of the source because only the temperature dependence of the number of excited carriers at the main peak is required. Since a low-pass filter was used, the spectral distribution of the light-source intensity was modified as shown by the dashed curve in the figure. The apparent photoconductive response due to the excitation of 1s electrons to the con-

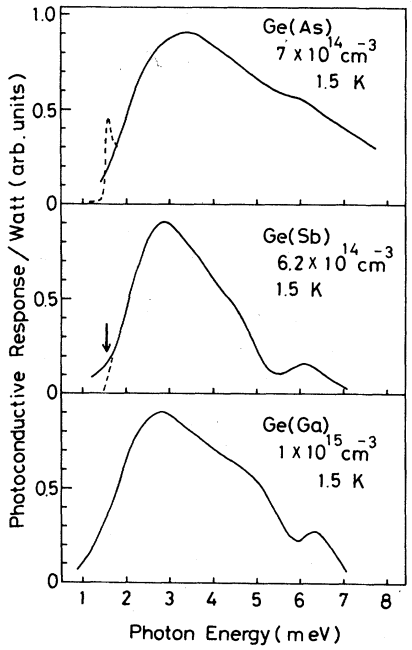

FIG. 1. Submillimeter photoconductivity spectra of doped germanium crystals. The dashed curve in the uppermost part is a reproduction of the result reported by Gershenzon, Gol'tsman, and Mel'nikov (Ref. 1). The arrow in the middle part indicates the electron affinity of the trapping state obtained from the temperature dependence of the photoconductivity.

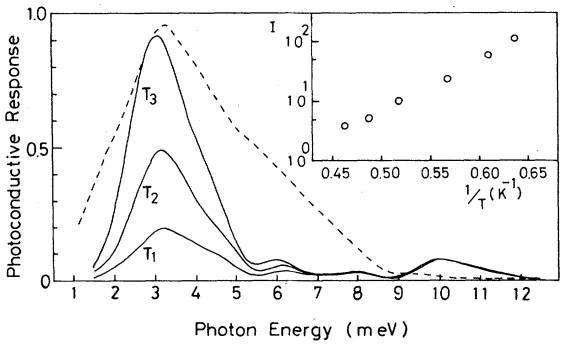

FIG. 2. The temperature dependence of the submillimeter photoconductive response in Sb-doped Ge. T_1 = 1.76, T_2 = 1.64, and T_3 = 1.57 K. The dashed curve indicates the spectral distribution of the light-source intensity modified by a low-pass filter. The inset shows a plot of the relative photoconductive response at the main peaks (I) against reciprocal temperature.

duction band at 10 meV is observed as a relatively weak peak and the peak near 3 meV appears as a relatively strong one in the figure.

Spectral humps can be seen also at 4.5, 6, and ~8 meV in Fig. 2. Although the ~8-meV hump is believed to be due to the so-called "photo-thermal ionization"[3] of the donors, the origin of the other humps is uncertain.

The inset in Fig. 2 shows a plot of the relative photoconductive response (which is proportional to the number of the excited carriers) at the main peaks (~3 meV) against reciprocal temperature. The photoconductivity increases exponentially with decreasing temperature.

Let us assume that the conduction-band electrons are generated from the donor ground states by the room-temperature background radiation, that they exist in a steady state, and that the electrons trapped in the trapping centers are in thermal equilibrium with the conduction electrons. Thus, the density of the electrons in trapping centers, n_T, is given by

$$\left(\frac{N_T}{n_T}\right) = 2\left(\frac{2\pi m_D^* kT}{h^2}\right)^{3/2} \times \left(\frac{1}{n_c}\right)\exp\left(\frac{-W}{kT}\right) + 1 . \quad (1)$$

Here N_T is the density of trapping centers, n_c is the density of conduction electrons, W is the energy separation between the bottom of the conduction band and the trapping center, and m_D^*, the density-of-states effective mass, is given by

$$m_D^* = (m_l^* m_t^{*2})^{1/3}, \quad (2)$$

where m_l^* is the longitudinal conduction-band mass and m_t^* is the transverse mass.

For the Ge sample with 6.2×10^{14} cm^{-3} Sb, the resistivities and the Hall coefficients were also obtained as a function of temperature. The carrier density in the conduction band under illumination of background radiation is 7.56×10^{8} cm^{-3} at 2.16 K and 4.91×10^{8} cm^{-3} at 1.57 K, while the Hall mobility is almost independent of temperature, $\sim 2.0\times10^{5}$ cm^2/V sec.

Using Eq. (1) we estimate the electron affinity of the trapping center, W, to be 1.56 meV. This value is very close to the photoconductivity threshold obtained by extrapolating the low-energy slope of the main peak in the middle curve in Fig. 1. With the assumptions that the trapping centers are the D^- states and that $N_T = N_D$ (the donor density) and by use of the known effective masses of Ge, we can calculate the number of trapped electrons in the above condition to be 3.3×10^{13} cm^{-3} at 1.57 K. Thus, these experiments confirm that the observed center must be a trapping center of some kind.

High-energy electron bombardment of Ge generally increases the density of acceptors so that in n-Ge the crystal becomes strongly compensated. The photoconductivity experiment was repeated with an electron-irradiated Ge(As) sample with compensation ratio $k = \sim 0.4$ and donor density $N_D = 6\times10^{14}$ cm^{-3}. It was very difficult to observe the photoconductivity signal with the sample. However, when the sample was illuminated by relatively weak radiation corresponding to the interband transition, the photoconductivity recovered. This phenomenon can be interpreted as follows: The trapping centers cannot bind electrons in the presence of the strong electric field due to the ionized donors and acceptors, while under the interband illumination, electrons and holes are created and they neutralize the ionized donors and acceptors and the response recovers.

Though the above experiment suggests a trapping center such as the D^- states, the deduced electron affinity (1.56 meV) is about three times as large as that predicted for the D^- state by Lampert[4] and others from a simple analogy to the H^- state[5] assuming a simple isotropic energy band. Apart from this discrepancy, however, our results are consistent with those expected for the D^- state and also with the results obtained by Gershenzon, Gol'tsman, and Mel'nikov[1] except for the spectral peak energy and the spectral shape. Consequently, it is most probable that the trapping center is indeed the D^- state.

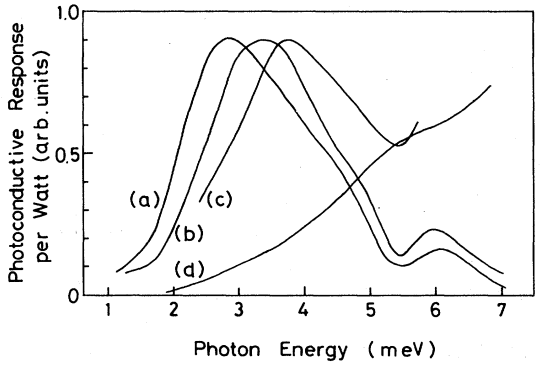

FIG. 3. The impurity concentration dependence of the submillimeter photoconductivity spectra of Sb-doped Ge at 1.5 K. The impurity concentrations are (curve *a*) 6.2×10^{14} cm^{-3}, (curve *b*) 2×10^{15} cm^{-3}, (curve *c*) 1.1×10^{16} cm^{-3}, and (curve *d*) 3.7×10^{16} cm^{-3}.

The following experiment tends to support this conclusion.

Figure 3 shows the change in the photoconductivity spectra with increasing impurity concentration. The position of the peak is seen to shift to higher energies.

Such a shift has been predicted by Nishimura[6] for the D^- state. He showed, by using the tight-binding approximation, that the interaction between the D^- states leads to the formation of the D^- band, and the energy separation between the conduction band and the D^- band spreads with increasing density of neutral donors.

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Combined Resonances in Hot-Electron Magnetophonon Oscillations in InSb

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A full series of combined cyclotron- and spin-resonance transitions is observed in magnetophonon oscillations in n-InSb under hot-electron conditons. These originate from the emission of LO phonons. Probabilities of combined resonances induced by polar and nonpolar coupling with optical phonons are calculated for the spin-orbit interaction mechanism.

The magnetophonon effect, also known as Gurevich-Firsov oscillations,[1] serves as a powerful tool in the investigations of band structure and its behavior in a magnetic field, as well as of the nature of electron-phonon interaction in semiconductors. The magnetoresistance oscillations, due to inelastic transitions induced by optical phonons between Landau sub-bands with the same spin orientation, occur at magnetic fields corresponding to the condition $N\omega_c = \omega_L$, $N = 1, 2, \ldots$, with $\omega_c = eH/m^*c$ and ω_L denoting cyclotron frequency and phonon frequency, respectively. The results obtained by some authors on InSb and InAs,[2] and previously attributed to transitions involving a change in spin orientation, can be shown to occur at the wrong fields for spin-flip transitions if the band nonparabolicity is taken into account, but at the correct field for the first extremum in a series $N\omega_c = 2\omega_L$.[3,4] The latter condition has been interpreted by Stradling and Wood[4] as due to two-phonon scattering processes. It seems, however, that the additional extrema can be reinterpreted in terms of one-phonon pseudoresonances proposed by Peterson,[5] which occur at $(2N+1)\omega_c = 2\omega_L$. Recently Morita, Takano, and Kawamura[6] reported combined-resonance transitions in the transverse photoconductivity of InSb, not attempting, however, to propose the physical mechanism responsible for the spin-flip.

Here we report direct evidence of phonon-induced electron transitions between Landau subbands with different spin orientations, observed in the magnetophonon effect under hot-electron