often observed in the resistivity-versus-temperature curves at the helium $\lambda$ point. If the field is chosen so that the minimum occurs at a slightly higher temperature than the $\lambda$ point, the resistivity is often observed to decrease as the temperature is lowered through the $\lambda$ point. This is just the opposite behavior which one would expect if the high thermal conductivity of the superfluid brought the sample into closer equilibrium with the bath and hence lowered the sample temperature discontinuously.[10] However, it seems possible that such a result could occur if the superfluid helium shorts out the heat currents within the sample. If such an explanation is correct, the heat currents in the helium should have a larger effect in a thin sample than in a thick one. We plan to investigate this thickness dependence and to make a more detailed study of the effect of mean free path on the thermal dissipation.

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[10]A similar behavior is discernible in the thinner $Pb_{95}Tl_{05}$ sample in Fig. 2, where in the absence of a minimum the resistivity is constant from $t = T/T_c \sim 0.5$ to $t \sim 0.3$, but drops discontinuously at the $\lambda$ point $t = 0.304$.

## OPTICAL DETECTION OF SURFACE STATES ON CLEAVED (111) SURFACES OF Ge

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Optical absorption of a cleaved surface of germanium shows a band at energies smaller than the gap, that is removed when the surface is oxidized. The band is assumed to be due to optical excitation of a surface state practically coincident with the top of the valence band to a set of states 0.16 eV below the bottom of the conduction band.

In recent years, the improvement of theoretical techniques has made possible realistic calculations of the distribution of surface states in semiconductors and insulators.[1-4] Their energy in the forbidden gap, however, depends in a critical way on the termination of the potential at the surface, on the structure of the surface planes, and on various integrals involving both bulk and surface parameters.

A major difficulty is the lack of reliable experimental data to compare with the theoretical estimates, especially in the case of cleaved surfaces. Moreover, the few experimental results known to date are of a rather indirect nature and often of nonunivocal interpretation.[5]

In this Letter we present a direct measurement of the optical absorption due to the presence of a band of surface states below the bottom of the conduction band on cleaved (111) surfaces of germanium. The number of surface states on clean germanium can be so large that a beam of monochromatic light undergoing total internal reflection on a cleaved surface shows a detectable increase of intensity when the surface is slowly oxidized.

Figure 1 shows the variation

$$\frac{\Delta I}{I} = \frac{I_{\text{oxidized}} - I_{\text{clean}}}{I_{\text{oxidized}}} \qquad (1)$$

of the intensity of light as a function of the energy of the photons.[6] The path of light which undergoes five total reflections on the cleaved surface is shown in the insert of Fig. 1.[7] Preliminary experiments show that similar results are obtained also in the case of silicon.

Measurements were taken in nearly intrinsic Ge; the clean surface was obtained by cleaving the crystal in ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr) with an externally operated hammer. Complete oxidation of the surface (as detected by the limiting value of $\Delta I/I$) was reached after an exposure of about $4 \times 10^{-4}$ Torr min.[8]

At the end of the experiment it was checked

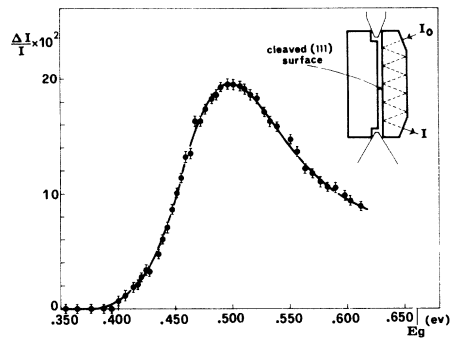


FIG. 1. Variation of the intensity of light totally reflected at a cleaved surface of intrinsic Ge at room temperature after the oxidation of the surface, as a function of the energy of the photons: $\Delta I/I = (I_{\text{oxidized}} - I_{\text{clean}})/I_{\text{oxidized}}$. The path of the light is also shown in the insert of the figure.

that light reflects totally at the cleaved surface and that "leakage" of light (if present at all) gives a contribution to the detected intensity smaller than $10^{-3}$. In such conditions, the increase of transmitted light intensity at energies smaller than those of the indirect gap is certainly due to the disappearance of abosrbing centers (situated in the forbidden gap) brought about by the oxidation of the surface. In order to clarify the mechanism of light absorption by surface states, the position of the Fermi level at the surface was measured, in a sample treated in the same way, by following the change of surface conductance (down to the conductivity minimum) during exposure to oxygen and wet oxygen. Assuming the experimental values of Missman and Handler[9] for the surface mobility, the Fermi level at the surface is found to lie $12kT$ below the midgap; i.e., the surface is found to be almost $p$-type degenerate in agreement with earlier measurements.[9]

Various processes could in principle explain the results of Fig. 1: (i) optical excitation of an electron in a surface state having an excited state in the forbidden gap, (ii) optical transitions from the valence band to an empty surface state located in the gap, (iii) optical transitions from a full surface state in the gap to the empty levels of the conduction band, and (iv) free-hole absorption in the surface $p$-type layer.

Hypothesis (iv) does not seem consistent with the known shape of the free-hole absorption spectrum in bulk Ge. On the other hand, the strength of the free-hole absorption to be expected for a clean surface of Ge (as inferred from the known value of the surface potential, $-12kT$, and the optical cross section for free-hole absorption[10]) is at least ten times smaller than that shown in Fig. 1. Also against hypothesis (iv) is the observation that similar results are obtained in silicon.

Hypothesis (iii) is ruled out by the experimental value of the Fermi level at the surface. The states in the gap are practically empty except for a narrow set near the top of the valence band (whose position is far too low to account for the observed results).

In case of process (ii) the absorption coefficient $\alpha(\omega)$ is given by

$$\frac{\alpha(\omega)}{P(\omega)} \propto \int_0^{\hbar\omega} g(E)(\hbar\omega - E)^{1/2} dE, \qquad (2)$$

where $E$ is measured from the top of the valence band, $g(E)$ is the density of surface states at energy $E$, and $P(\omega)$ is the transition probability at the frequency of the photon. The density of states in the valence band has been assumed, as usual, proportional to $|E|^{1/2}$.

If $P(\omega)$ is a constant, Eq. (2) gives rise to an absorption monotonically increasing with frequency and with a sharp threshold. In any case it appears difficult to fit the peaked curve of Fig. 1 with Eq. (2).[11]

The most reasonable hypothesis seems then to be (i), i.e., optical transitions from a narrow band of occupied surface levels near the top of the valence band to a set of states below the bottom of the conduction band. Since the Fermi level at the surface is practically coincident with the top of the valence band, the curve of Fig. 1 is proportional to the density of surface levels measured from the top of the valence band. It seems then safe to conclude that the experimental results of Fig. 1 give evidence of the existence, on cleaved (111) surfaces of Ge, of a band of states centered approximately 0.16 eV below the bottom of the conduction band to which transitions can be made from surface states localized near the top of the valence band.[12] Such a model bears some analogy with the theoretical results of R. O. Jones,[3] who shows the presence of two bands of surface states partially overlapping the valence and conduction bands on (110) surfaces of diamondlike structures.

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[8]This value is in agreement with that reported by H. E. Farnsworth and R. E. Schlier [J. Chem. Phys. 30, 917 (1959)] for (111) surfaces.

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[12]It must be pointed out that also in the case of hypothesis (ii) the results show the existence of a band of levels at energies $\leq 0.24$ eV below the bottom of the conduction band.

## OPTICAL REFRIGERATION IN Nd-DOPED YTTRIUM ALUMINUM GARNET

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Optical refrigeration has been observed by subjecting single crystals of yttrium aluminum garnet and Nd-doped yttrium aluminum garnet to intense 1.064-$\mu$ laser radiation. In addition to this first observation of optical refrigeration, the present experiments yield a very accurate value for the fluorescent quantum efficiency of Nd-doped yttrium aluminum garnet.

A luminescence process in which the excitation energy is less than the emitted photon energy can be regarded as a refrigeration or heat-extraction cycle, since a certain amount of internal energy must be supplied to the radiation field. Although this type of refrigeration in photo- and electroluminescent systems has been discussed theoretically by several investigators,[1-4] there seems to be no prior report of an experimental study. An intense laser beam will be an efficient excitation source for such an optical refrigerator. In this Letter, an optical refrigeration experiment is reported in which yttrium aluminum garnet doped with neodymium (YAlG:$Nd^{3+}$) is employed both as the refrigerator and laser material.[4]

As shown in Fig. 1, the refrigerator crystal system [Fig. 1(b)], which is made to absorb the laser radiation from the laser-crystal system [Fig. 1(a)], cools down by anti-Stokes fluorescence. In order to observe net cooling, the possible heating mechanisms of Stokes fluorescence, nonradiative transitions [see Fig. 1(c)], and the absorption of laser radiation by impurity ions in the refrigerator crystal are required to be weak compared with the cooling by anti-Stokes fluorescence. In the present experiments, using YAlG :Nd, heating due to absorption by small trace impurities, probably $Dy^{3+}$, exceeded the cooling by the $Nd^{3+}$ ions and net cooling was not achieved. However, by measuring the reduced, nonlinear, power-dependent heating in Nd-doped YAlG as compared with the linear, power-dependent heating in undoped YAlG, the effects of cooling or refrigeration by anti-Stokes fluorescence in $Nd^{3+}$ have been successfully observed.

For steady-state conditions, the heat-extraction rate per unit volume by optical refrigeration

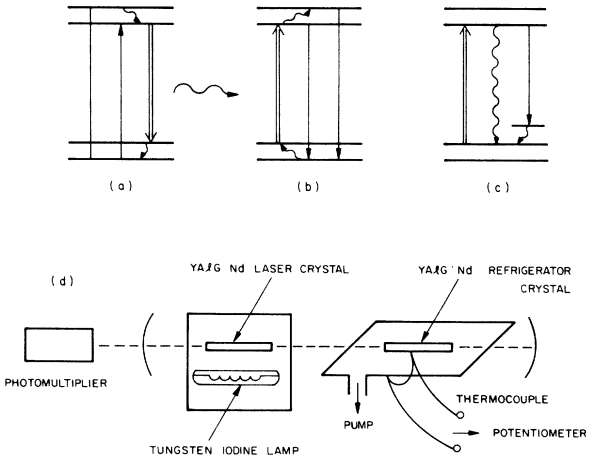


FIG. 1. Schematic description of (a) laser cycle, (b) refrigeration cycle, (c) possible mechanisms of heating, and (d) experimental arrangement.