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Specific heat of silicon in the millidegree region

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The low lattice specific heat of silicon in the cryogenic regime makes it eminently suitable for particle bolometry. In fact, the lattice specific heat becomes so low in the millidegree regime that electronic contributions from 10^{14} cm^{-3} electrically active impurities can exceed it. Various mechanisms that can produce an electronic specific heat are discussed quantitatively and compared with the lattice specific heat. It is concluded that with moderate care the electronic effects can be reduced to a level that will not interfere with particle bolometry in the millidegree range.

INTRODUCTION

Silicon has a high Debye temperature and a specific heat that becomes very small at temperatures below 1 K. Measurements to 50 mK find a specific heat of only $10^{-10}k$ per atom of silicon, in good agreement with the accepted Debye temperature, $\Theta_D = 636$ K (k is the Boltzmann constant).[1] The low specific heat makes silicon uniquely suitable for particle bolometry, and the measurement of the temperature increase of small pieces of silicon caused by the deposition of energy by a single charged particle at around 1 K is an established technique.[2] It has recently been suggested that large masses of silicon might be used for bolometry in the case of weakly interacting particles, where a substantial volume is needed to provide useful probability of an event.[3] However, the heat capacity of a large volume of silicon reduces the sensitivity of the technique. Thus, bolometry with a large volume can only be used at temperatures much below 1 K, where the lattice heat capacity is again small compared to the energies of particles of interest.[3] For example, deposition of 100 MeV of energy by an energetic particle could raise the temperature of 1 kg of pure silicon from 5 to 20 mK. Measurement of the temperature increase detects the particle.

However, even the purest silicon contains measurable amounts of other elements. Donor and acceptor impurities, those in group V and III, contribute holes and electrons to the silicon and modify the distribution of electronic states in the vicinity of the energy gap. Large effects are produced at high concentrations. Thermal excitations among the electronic states can contribute to the specific heat.[4,5] Although these contributions are small at low concentrations, they may be significant in the millidegree regime because of the very low lattice heat capacity. Here we estimate the magnitude of the contribution of various electronic excitations to the heat capacity of silicon at low temperatures and low-impurity concentrations. Measurable effects of this kind may not only guide the selection of materials for bolometry, but also constitute new tools for the investigation of low concentrations of electrically active impurities.

Our purpose here is to identify possible effects, and the differences among the various electrically active impurities will be ignored and the average values of donor and acceptor parameters will be used. It should be possible to use silicon with impurity concentrations less than 10^{14} cm^{-3}, and such concentrations will be used in examples.

I. IMPURITY BANDS

The formation of an impurity band is perhaps the best-known electronic effect of dilute concentrations of impurities at low temperatures. Extensive measurements of impurity conduction were reported by Ray and Fan[6] and a 1984 review of impurity bands in silicon covers many recent developments.[7] The electronic states in the impurity band are localized and their distribution follows the distribution of the electrostatic potential[8]

$$F(\psi) = (e/\gamma\pi^{1/2})\exp[-(e\psi/\gamma)^2] \ . \tag{1}$$

Here ψ is the potential, e is the electronic charge, and γ is defined by

$$\gamma = 0.42(e^2/\kappa)N^{1/3}K^{1/4} \ . \tag{2}$$

N is the impurity concentration, K is the fraction of impurity that is compensated, and κ is the dielectric constant of the semiconductor. The density of states in terms of the electronic energy E is

$$n(E) = (N/\gamma\pi^{1/2})\exp[-(E/\gamma)^2] \ . \tag{3}$$

The Fermi level ξ is determined by the condition that the compensation is represented by empty states at the top of the band

$$K = \int_{\xi}^{\infty}(1/\gamma\pi^{1/2})\exp[(-E/\gamma)^2]dE \ . \tag{4}$$

For small compensation

$$K = (\gamma/2\xi\pi^{1/2})\exp[-(\xi/\gamma)^2] \tag{5}$$

is a good approximation. The density of states at the Fermi level is therefore

$$n(\xi) = (2\xi K/\gamma^2)N \tag{6}$$

and the specific heat per unit volume is

$$C = (\pi^2k^2T/3)(2\xi K/\gamma^2)N \ . \tag{7}$$

In Eq. (7) ξ is to be determined by solving (5).

Examples of the specific heat calculated from Eq. (7) are compared with the lattice specific heat C_L in Fig. 1. It is seen that C_{IB} is larger than C_L below 15 mK when $N=10^{13}$ cm^{-3} and below 30 mK when $N=10^{14}$ cm^{-3} if $K=0.1$.

Thus, the impurity band heat capacity appears large enough to affect bolometry below 100 mK. It is unlikely that any effects would actually be observed, however. The excitations in the impurity band that absorb the thermal energy involve motion from one physical location to another. Extrapolations of the resistivities measured at concentrations around 10^{17} cm^{-3} to 1 K yields values exceeding 10^{30} Ω cm. It can be estimated that such a resistance means that the mean time for a transition between states is greater than 10^{20} s. Much longer times would be found at 0.1 K and concentrations of 10^{14} cm^{-3}; effects would be unobservable on an experimental time scale.

II. SCHOTTKY SPECIFIC HEAT

The remaining effects to be treated arise from small splittings of degenerate energy levels. The specific heat arising from the excitation of a particle between two energy levels is known as a Schottky specific heat.[9] If the difference in energy of the two levels is Q, then the ratio of the population of the two levels is $e^{-Q/kT}$. The energy of the system above the ground state is

$$U_S=Q/[1+\exp(Q/kT)] \ . \tag{8a}$$

The maximum of U_S regarded as a function of Q at fixed T occurs at $Q/kT=1.2785$ and is $U_S=0.2785kT$. The specific heat is found by differentiating Eq. (8a):

$$C_S=k(Q/kT)^2\exp(Q/kT)/[1+\exp(Q/kT)]^2 \ . \tag{8b}$$

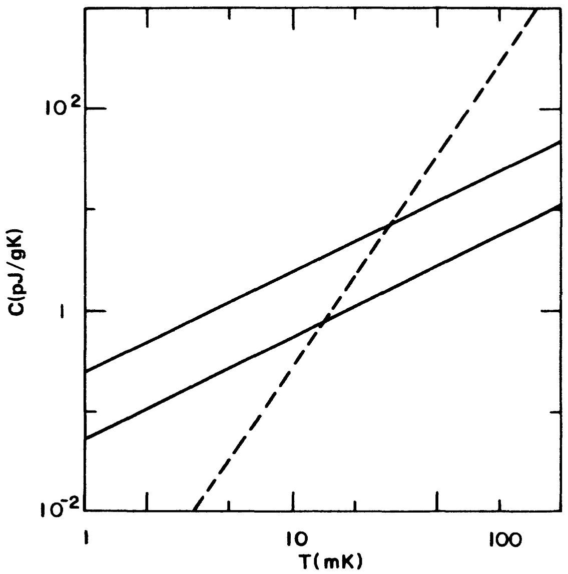

FIG. 1. Comparison of the specific heat of the silicon lattice (dashed line) with the specific heat of an impurity band according to the model of Eqs. (1)–(8). $N=10^{13}$ cm^{-3} or 10^{14} cm^{-3} and $K=0.1$ in these examples.

The maximum of the specific heat is found at $T=0.417Q/k$ and is $0.439k$. At high temperatures, $Q/kT \ll 1$, $U_S \approx Q/2$.

A. Strained acceptors

The ground state of acceptors in silicon is degenerate and is split into two levels by strain.[10] The magnitude of splitting is approximately 10 eV times the strain.[10] Thus excitation energies of order 10^{-2} K are produced by strains of 10^{-7}. A concentration of two-level centers of 10^{13} cm^{-3} with energy separation 10^{-6} eV dominates the lattice specific heat between 1 and 25 mK and adds a heat capacity of about 2×10^5 MeV/kg K in this range. Strains of this magnitude might be hard to avoid; the strain at the bottom of a 1-kg cube of silicon resting on a flat surface is about 0.3×10^{-7}. Apparently this acceptor heat capacity could be eliminated by applying a stress large enough to split the energy levels by an amount k times the maximum temperature of interest, but one might be concerned about the heat capacity of the apparatus used to apply the stress. It could also be avoided by insuring an excess of donor impurities. This effect has previously been discussed and compared with the lattice specific heat.[11]

B. Heitler-London states

The wave functions of electrons trapped on donors (or holes trapped at acceptors) are hydrogenlike in a first approximation. When the hydrogenic wave functions overlap, a splitting of their degeneracy in the way originally described by Heitler and London (HL) occurs.[12,13] Heitler and London calculated the energy levels of a pair of hydrogen atoms by the variational method with a trial function of the form

$$\Phi=\alpha\phi_A(1)\phi_B(2)+\beta\phi_A(2)\phi_B(1) \ . \tag{9}$$

Here $\phi_A(1)$ is, e.g., the hydrogenic wave function of electron 1 on donor A. The splitting of the energy levels is a function of the ratio of the distance between the hydrogenic centers, R, to the Bohr radius of the hydrogenic functions a, and can be written in the Heitler-London approximation as

$$Q(\rho)=(e^2K a)f(\rho) \ . \tag{10}$$

Here $\rho \equiv R/a$.

In the case of dilute concentrations of impurities in semiconductors, large values of ρ are of interest. For example, the average distance from a donor to its nearest neighbor is $0.554N^{-1/3}=55$ nm if $N=10^{15}$ cm^{-3}. A typical value of a in silicon is 1.9 nm, or $R/30$. The donor pairs of interest in the present problem are not the average pair; however, even for the pairs that contribute to specific heat at millidegree temperatures $R/a>5$. The function $f(\rho)$ has been evaluated for $\rho \gg 1$ by Herring and Flicker,[14] who showed that

$$Q(\rho)=4E_{\mathrm{H}}C_1\rho^{5/2}e^{-2\rho} \ . \tag{11}$$

Here E_{H} is the hydrogen rydberg and $C_1=0.821$.

The probability that the nearest neighbor of a donor lies between R and $R+dR$ (ρa and $\rho a+a\,d\rho$) is

$$P_1(\rho)=4\pi N a^3\rho^2\exp[-(4\pi/3)Na^3\rho^3]\ . \tag{12}$$

The average contribution of a donor pair to the specific heat is thus

$$C_{\mathrm{HL}}=k\int_0^\infty P_1(\rho)\frac{(Q/kT)^2 e^{Q/kT}}{(1+e^{Q/kT})^2}d\rho\ . \tag{13}$$

Q is expressed as a function of ρ by Eq. (11). Most of the contribution to C_{HL} comes from the vicinity of the maximum of the specific-heat function in the integrand. Write

$$d\rho=dQ/(dQ/d\rho)=dQ/Q[(5/2\rho)-2]\ . \tag{14}$$

An adequate approximation to C_{HL} is obtained by regarding $P_1(\rho)$ and $dQ/d\rho$ as slowly varying and evaluating them at ρ_m, the value of ρ that corresponds to the maximum of the specific-heat function, $Q=2.40kT$. ρ_m can be determined by solving Eq. (11). Furthermore, the exponential factor in Eq. (12) is very close to unity at the low concentrations of interest here. Thus it is found that

$$C_{\mathrm{HL}}=4\pi N a^3\rho_m^2[2-(5/2\rho_m)](\ln 2)k\ . \tag{15}$$

Equation (15) is the specific heat per donor pair and must be multiplied by $(N/2)$ to obtain the specific heat of a unit volume of silicon.

The value of C_{HL} obtained from Eq. (15) with $N=10^{14}$ cm^{-3} is shown in Fig. 2. It is seen that C_{HL} dominates C_L below 5 mK at a concentration 10^{14} cm^{-3}. Values $E_{\mathrm{H}}=0.04$ eV and $a=1.9$ nm were used in this example.

C. Molecule-ion states

A splitting of the symmetrical and antisymmetrical energy levels similar to that discussed in the previous section also occurs in the case of one electron trapped on a pair of donors, the hydrogen molecule-ion analog. The existence of such singly occupied pairs at low temperatures depends on compensation. The simplest reasonable treatment of the problem uses the variational method with wave functions of the form

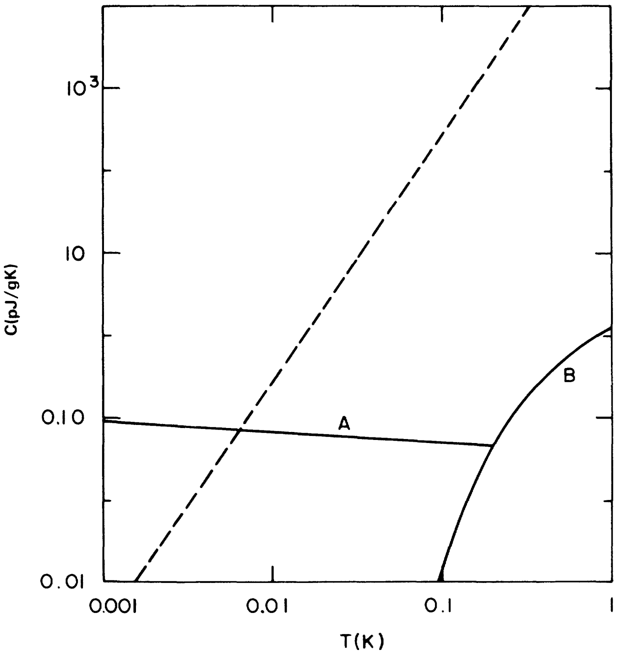

FIG. 2. Contribution of impurity pairs to the specific heat according to Eq. (15) (curve A) and Eq. (20) (curve B) compared with C_L.

$$\Phi=\phi_A\pm\phi_B\ . \tag{16}$$

When the distance between the donors is large, the difference in the energies of the two states is[14]

$$Q(\rho)=(4/e)E_{\mathrm{H}}\rho\exp(-\rho)\ . \tag{17}$$

The electric fields arising from the charged impurities that result from compensation will alter the energies of the wave functions on impurities A and B in Eq. (16), however. The small energy difference is only correctly described by Eq. (17) if ϕ_A and ϕ_B are nearly degenerate. To take account of the removal of degeneracy by the electrostatic potential, the contributions to the low-temperature heat capacity will only be counted when no other charged impurity is so close to the donor pair in question that its electric field can cause the energies of ϕ_A and ϕ_B to differ by more than Q. In other words, there can be no other charge within a distance X, when X satisfies

$$(e^2/\kappa X^2)R=Q(\rho)\ . \tag{18}$$

The probability that there is no charged donor within a radius X is

$$\begin{aligned}P_0(\rho)&=\exp[-(4\pi/3)KNX^3]\\&=\exp\{-(4\pi/3)KN[e^2a\rho/KQ(\rho)]^{3/2}\}\ .\end{aligned} \tag{19}$$

The average contribution of a singly occupied donor pair to the specific heat is

$$C_{MI}=\int P_1(\rho)P_0(\rho)C_S(\rho)d\rho\ . \tag{20}$$

Here $C_S(\rho)$ is to be obtained by using the $Q(\rho)$ of Eq. (17) in Eq. (8b). Both $P_0(\rho)$ and $C_S(\rho)$ in Eq. (20) vary rapidly with ρ and no simplification of the integral has been found. An example of C_{MI} obtained by numerical methods is shown in Fig. 2. C_{MI} is so small that a concentration of $N=10^{15}$ cm^{-3} was chosen for this example. even at this relatively high concentration C_{MI} is negligible compared to C_L, and it is concluded that C_{MI} is unimportant.

A question can also be raised about the effects of electric fields in compensated samples in the neutral donor molecule case of the preceding section. Electric fields do not remove the degeneracy of the Heitler-London basis functions, Eq. (9), but may change the value of the splitting from that given by Eq. (11).

D. Magnetic specific heat

Kobayashi *et al.*[4] found that there is a low-temperature Schottky specific heat in silicon doped with phosphorus donors in a magnetic field. The energy difference [Q in Eq. (8b)] is about $2\mu_B H$ and the concentration of specific-heat centers approached the concentra-

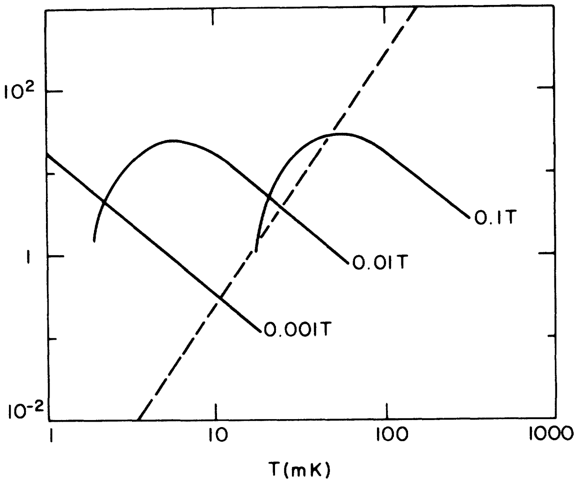

FIG. 3. The specific heat of 10^{13} cm^{-3} donors in various magnetic field, based on the results of Kobayashi *et al.* (Ref. 4).

tion of donors at low concentrations. For example, at a donor concentration of 10^{13} cm^{-3} and magnetic fields less than 0.05 T this magnetic Schottky specific heat would exceed the lattice specific heat below $T=0.16H^{0.4}$, where H is in tesla and T in K. Examples are presented in Fig. 3. Magnetic splitting of similar magnitude also occurs in acceptors, where it gives four levels that interact with the strain splitting of the ground state.[15]

III. ENERGY

Changes in temperature large compared to the initial temperature are often useful in bolometry. It is then more appropriate to think of the total energy U of the semiconductor, the integral of the specific heat. The results of the above sections are shown in this form in Fig. 4.

IV. OTHER IMPURITIES

The existence of carbon and oxygen atoms in concentrations up to 10^{18} cm^{-3} in silicon is common. However, not enough is known about the properties of these impurities to attribute any thermal effect to them or to exclude such effects. Some possibly relevant effects have been observed recently by Kleiman *et al.*[16]

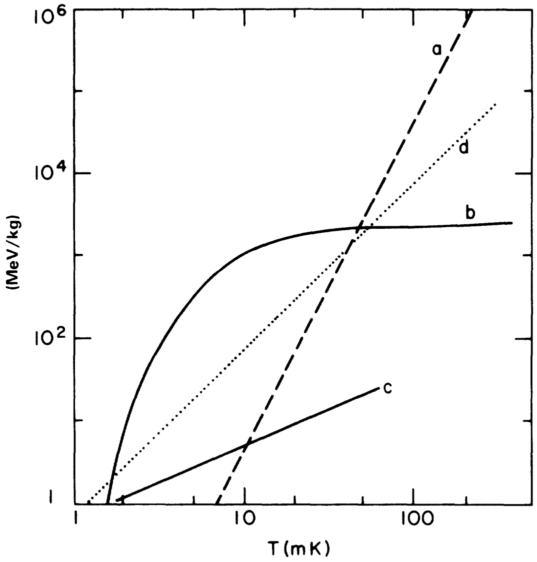

FIG. 4. The integral from 0 to T of various specific-heat contributions considered in the text; (a) the lattice energy, (b) the integrated magnetic specific heat for the case $N=10^{13}$ cm^{-3} and $H=0.01$ T. The energy for the case of 10^{13} cm^{-3} strained acceptors discussed in Ref. 11 is also closely represented by this line. (c) The energy of the hydrogen moleculelike pairs, $N=10^{14}$ cm^{-3}. (d) The result for the impurity band with $N=10^{14}$ cm^{-3}.

CONCLUSION

With ordinary care the electronic effects treated will not affect particle bolometry at temperatures above 10 mK. The largest effects found are those associated with the splitting of acceptor states by strain and of impurity levels by a magnetic field. The former can be avoided by the use of n-type material, the latter by separation of the bolometer from sources of strong magnetic fields. As discussed, the impurity band effects are not expected to be observable on any reasonable time scale. The H-molecule-like specific heat may be observable below 10 mK at a concentration of 10^{14} cm^{-3}.

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