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## Evidence for a Jahn-Teller Effect in *p*-Ge from Magnetothermal Conductivity Measurements

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The phonon scattering by shallow acceptors in Si has been observed to decrease rapidly with magnetic field at high fields and low temperatures. This is the behavior expected for the ground-state quartet of the undistorted site. The scattering by shallow acceptors in Ge is, however, almost independent of field, indicating a quite different ground-state structure. This is believed to be the result of a dynamic Jahn-Teller distortion.

In undistorted sites, the acceptor ground states of Ge and Si are both fourfold degenerate ( $\Gamma_8$ ). However, the states are known to be very strongly coupled to the lattice,<sup>1-4</sup> so that the possibility of a dynamic Jahn-Teller effect must be considered. This could lead to a complex spectrum of levels,<sup>5</sup> and the problem seems to be particularly interesting because the state should couple to the lattice only at wave numbers  $q$  less than  $(a^*)^{-1}$ , where  $a^*$  is the Bohr radius of the state, since at higher values of  $q$  the effect of strain is averaged out over the wave function.<sup>6</sup> In this Letter we report measurements of the magnetic field dependence of the thermal conductivity in Ge(Ga) and Si(B) which, together with earlier work, indicate that the structure of the acceptor state in Ge is more complex than the simple quartet structure described above, presumably because of a Jahn-Teller effect.

In the undistorted site, phonons of energy much less than that of the first excited state (80 K in

Ge, 330 K in Si) can only be scattered from transitions within the quartet—a wholly elastic process. If the degeneracy of the ground state is removed by a magnetic field, the conductivity should first fall as the level splittings become comparable to the dominant phonon energies ( $\sim 4kT$ ) and then rise rapidly when the splittings become  $\gg kT$ . However, if the ground state is more complex, the behavior could be quite different.

The specimens used in this investigation were grown by the Czochralski technique<sup>7</sup> and had hole concentrations of  $1.0 \times 10^{16} \text{ cm}^{-3}$  for Ge(Ga) and  $9 \times 10^{16} \text{ cm}^{-3}$  for Si(B). These both correspond to an average distance  $d \sim (8-9)a^*$  [ $a^*(\text{Ge}) \sim 37 \text{ \AA}$ ,  $a^*(\text{Si}) \sim 15 \text{ \AA}$ ] which is a compromise between the desire to have a high concentration and so a potentially large effect, and the need to keep  $d \gg a^*$  to avoid overlap between neighboring acceptors. The specimen dimensions were  $20 \times 3 \times 3 \text{ mm}^3$  with the axis along a  $\langle 110 \rangle$  direction, and the field was applied either parallel to this axis or, at

principal directions in the (110) plane, normal to it. The measurements were made in continuous field sweeps with the data recorded on an XY plotter. The carbon resistance thermometers used for measuring  $\Delta T$  and for temperature stabilization were placed out of the main field and shielded by Nb foil, or by Pb foil and a bucking coil, to avoid magnetoresistance effects. Further experimental details will be given elsewhere<sup>8</sup> together with the results of an investigation of the anisotropy effects.

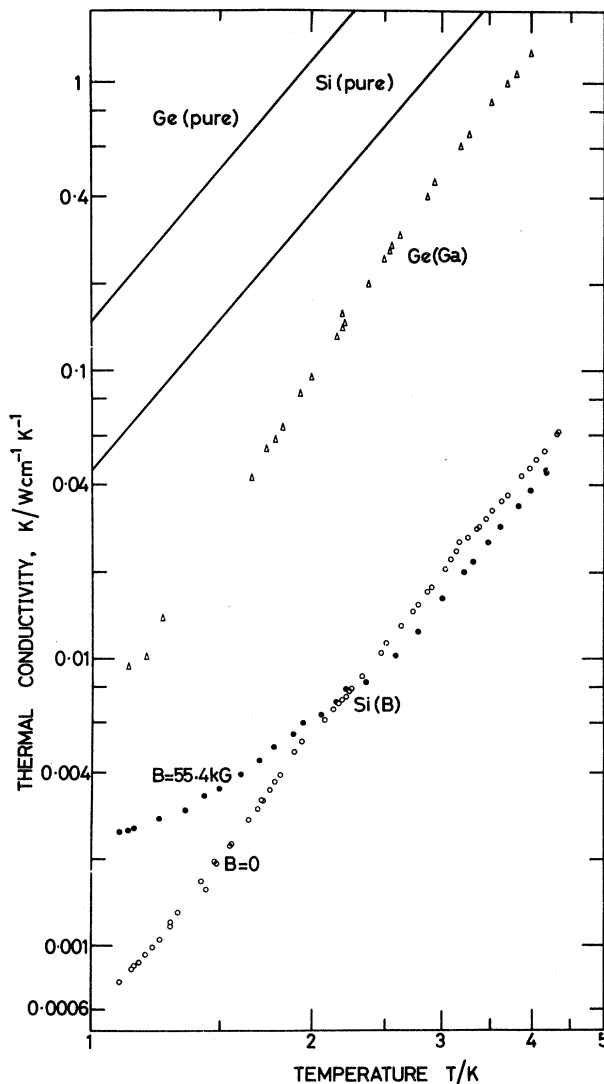


FIG. 1. The thermal conductivity of the Ge(Ga) specimen ( $p=1.0 \times 10^{16} \text{ cm}^{-3}$ ) in zero magnetic field and of the Si(B) specimen ( $p=9 \times 10^{16} \text{ cm}^{-3}$ ) in fields of 0 and 55.4 kG. The figure also includes curves for pure Ge and Si specimens of  $\chi$  section  $3 \times 3 \text{ mm}^2$  calculated assuming the only phonon scattering present is by boundaries.

The zero-field thermal conductivity data are shown in Fig. 1. They are very similar to those previously obtained for Ge(Ga)<sup>1</sup> and Si(B).<sup>2</sup> Conductivity values calculated for pure specimens of these dimensions where the scattering is by boundaries only are included for comparison. The figure also includes data for the silicon specimen taken in a magnetic field of 55 kG. The field was applied along a  $\langle 100 \rangle$  direction transverse to the specimen axis, although this is not significant since the anisotropy effects were found to be rather small. It is seen that at the higher temperatures, the field produces a small decrease in conductivity but at the lower temperatures there is a very considerable increase. The effect of field on the thermal conductivity is also shown in Fig. 2 and it is seen that the data are broadly consistent with the qualitative predictions of the quartet model given above. Thus the conductivity decreases to a shallow minimum and then rises rapidly at higher fields. If the reduced conductivities  $K/K_0$  are plotted against  $B/T$ , the minima all occur at the same value of  $B/T$  as might be expected, and indeed the curves differ by a few percent only over the whole range. The  $g$  values of the two Kramers doublets form-

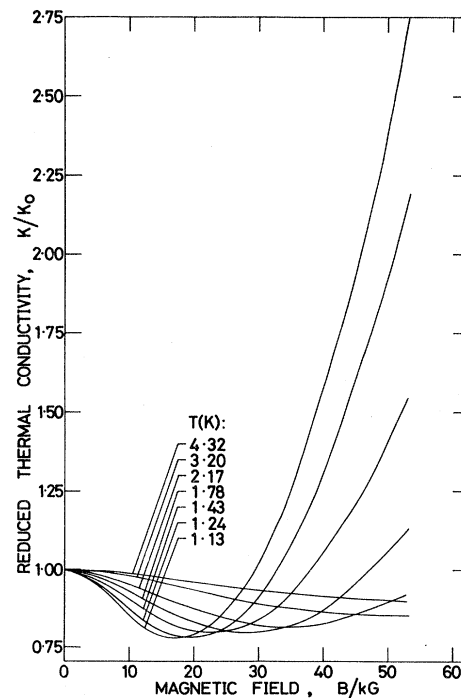


FIG. 2. The reduced thermal conductivity  $K/K_0$  of the Si(B) specimen at various temperatures as a function of magnetic field  $B$ , applied parallel to the specimen axis.

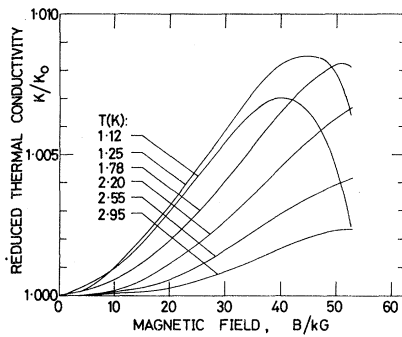


FIG. 3. The reduced thermal conductivity  $K/K_0$  of the Ge(Ga) specimen at various temperatures as a function of magnetic field  $B$ , applied parallel to the specimen axis.

ing the quartet do not appear to have been measured in unstrained Si (or Ge) but the values for Si calculated from effective-mass theory are  $g_{1/2} = 0.97$  and  $3g_{3/2} = 3.66$ .<sup>9</sup> These values could be used to make a quantitative comparison with a recent detailed theory of the field dependence based on the quartet model,<sup>10</sup> but in fact the agreement between the theory and the zero-field data is poor at the lower temperatures so that this has not been done. It would seem though that the scale of the effects is broadly in line with these  $g$  values.

The dependence of conductivity on field shown in Fig. 3 for Ge(Ga) is in striking contrast with the data for Si(B). (It is also very different from that observed in  $n$ -Ge,<sup>11</sup> but this is to be expected in view of the differences in the ground states.) The effect is of opposite sign, so that the conductivity is actually decreasing with field at the highest values of  $B/T$ , and the maximum change is less than 1% which is more than 2 orders of magnitude smaller than in Si. However, the theoretical  $g$  values<sup>9</sup> for Ge ( $g_{1/2} = -1.30$ ,  $3g_{3/2} = -0.57$ ) are appreciably smaller than in Si, and a comparison between the two sets of data might be more appropriate after the field axes have been scaled by a factor  $\sim 3$ . This procedure predicts that the conductivity of Ge(Ga) at 1.1 K and in 55 kG should be  $\sim 20\%$  less than its value in zero field<sup>12</sup> rather than  $<0.85\%$  more as observed. It is clear, therefore, that the data are inconsistent with the predictions of the degenerate quartet model.

Similar conclusions can be drawn from the results of a number of earlier investigations. In Sladek's work<sup>1</sup> on the thermal conductivity of Ge(Ga) between 1.8 and 4.2 K, the levels were split into two Kramers doublets by uniaxial com-

pression of up to  $1 \times 10^9$  dyn  $\text{cm}^{-2}$ . The stress was applied along a  $\langle 111 \rangle$  direction and is calculated to give rise to splittings of up to 25 K, but again little or no change in conductivity was observed. [For comparison it is noted that the splittings in a magnetic field which can give rise to scattering are  $\frac{1}{2}(g_{1/2} \pm 3g_{3/2})\beta B$  which in Ge correspond to 1.4 and 3.5 K in a field of 55 kG if the theoretical  $g$  values are used.] Measurements of thermal conductivity<sup>1,2</sup> and ultrasonic attenuation<sup>4</sup> of Ge(Ga) and Ge(In) in zero field are also inconsistent with the model as has been recently stressed by Suzuki and Mikoshiba.<sup>13,14</sup> They have shown that the quartet has a scattering cross section which should first increase as  $\omega^2$  and then fall rapidly above the cutoff at  $qa^* \sim 1$ . They observed that this is consistent with the thermal-conductivity<sup>1,2</sup> and heat-pulse data<sup>3</sup> at the higher frequencies  $q > (a^*)^{-1}$  but that it severely underestimates the scattering found at lower frequencies in both thermal conductivity<sup>1,2</sup> and ultrasonic data.<sup>4</sup> This is most noticeable in Ge where the thermal-conductivity data show that the scattering continues to increase with decreasing frequency even at  $\omega \sim 1.5 \times 10^{11}$   $\text{sec}^{-1}$  which is nearly an order-of-magnitude lower than the frequency  $\sim v/a^*$  at which it should start to decrease ( $v$  is the mean phonon velocity).

The zero-field conductivity data could possibly be accounted for by strain splittings of  $\sim 0.1$  K.<sup>15</sup> However, to explain the very small effects in the present work, the strain splittings of the acceptors responsible for most of the scattering would have to be very much larger than those produced by the magnetic field, say  $\geq 10$  K, and it would then be very difficult to account for the magnitude and temperature dependence of the conductivity below 2 K. This can be seen in the detailed calculations<sup>10</sup> which show that the conductivity would have a very marked change in slope at  $\geq 2$  K and would be an order of magnitude larger than that observed at 1 K. The interpretation of Sladek's data which would imply strain splittings appreciably greater than 25 K would be even more difficult. We conclude that the ground state must be more complex, presumably as a result of a dynamic Jahn-Teller effect.

We have deferred until this point any discussion on the recent work by Ishiguro, Fjeldly, and Elbaum,<sup>16</sup> since it has been shown to be consistent with the quartet model if some strain splitting is included. The measurements were of the effect of compressional stress applied along the  $[111]$  direction on the attenuation of heat pulses

in Ge(Ga). Stresses of comparable size to those used by Sladek were applied, and the principal difference is that the effective temperatures of the pulses were somewhat higher; the data shown for a specimen similar to those used in the thermal conductivity work were for 10.3 K pulses. The attenuation was observed to decrease by a factor of 2.5 in the highest stress. This very marked difference in behavior between the heat-pulse and thermal-conductivity work is most interesting and must presumably be explicable in terms of a Jahn-Teller theory. For the present we can only offer the comment that, although the difference in frequency of the phonons used is not great, it spans the  $qa^* \sim 1$  region.

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