Stress dependence of the thermal conductivity of Cr-doped GaAs

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Thermal-conductivity measurements under uniaxial stress on GaAs containing Cr^{3+} show that the ion is very sensitive to both E and T_2 strains. This is most unusual for strongly coupled Jahn-Teller ions and supports the existence of orthorhombic wells. The tunneling frequency between them is estimated at 300 GHz.

EPR spectra attributed to Cr^{3+} ions in GaAs show orthorhombic symmetry[1] and the authors concluded[2] that this is the result of a strong Jahn-Teller effect involving coupling to both E and T_2 modes. In this situation, provided the anharmonicity quadratic coupling is sufficient, the Jahn-Teller wells should be orthorhombically placed, that is, along the six $\langle 110 \rangle$ directions.[2] This behavior is very unusual and the first EPR evidence was not universally accepted[3] presumably because of the complication that the EPR transition frequency is probably comparable or less than the splittings due to random strains. A more critical test of the coupling is provided by the movement of the energy levels under applied stress. If they are very sensitive to $\langle 111 \rangle$ stress, then the Jahn-Teller wells cannot lie along tetragonal directions (the usual situation) since these make equal angles to $\langle 111 \rangle$, and trigonal directions can similarly be eliminated by sensitivity to $\langle 001 \rangle$ stress. An equivalent argument is that, for strong Jahn-Teller effects, the Ham reduction factors $\kappa(T_2)$ and $\kappa(E)$ vanish for E (tetragonal wells) and T_2 mode coupling (trigonal wells), respectively. If the levels are sensitive to both types of stress, there has to be similar Jahn-Teller coupling to both E and T_2 modes. EPR does not seem to be a good method for making this test as the signal amplitude appears to be very much less sensitive to $\langle 111 \rangle$ stress[2] and, while the authors accounted for this in terms of changes in linewidth, it could of course also indicate T_2 quenching. Indeed, the authors note that their clearest evidence for T_2 coupling comes from the differences in the effects of $\langle 001 \rangle$ (E) stress and $\langle 110 \rangle$ $(E+T_2)$ stress. Nevertheless, because of the possible complications of interpretation due to random strains in these different samples, it seemed very desirable to demonstrate the sensitivity of the level structure to both E and T_2 stresses applied separately. We have done this by investigating the effect on the thermal conductivity of Cr-doped GaAs of uniaxial stress applied along $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions.

Cr ions in GaAs give rise to strong phonon scattering at several frequencies up to 1000 GHz.[4,5] Scattering at $\lesssim 5$ GHz, which only occurs in n-type and semi-insulating (SI) material, is attributed to substitutional Cr^{2+}, and that at 21 and 690 GHz, with somewhat weaker processes at ~80, 150, and 400 GHz, only occurs in SI and p-type material and has been attributed to substitutional Cr^{3+}.[4] (Cr^{4+} has a $^3A_2$ ground state and so cannot scatter phonons strongly.) Above 1 K, the thermal resistivity is determined by the phonon scattering at 150, 400, and 690 GHz and movement of the levels causing this scattering is likely to have a profound effect on the thermal conductivity. The ten samples examined were undoped (GA803), n type (GA785), SI(TI4a_1, a_2, TI5, GA735a_2,e), and p type (GA781,a,b,c), and their details are given in Ref. 4. The doped samples contained ~1 ppm of Cr and some were codoped with Si or Zn. The measurements were made from 2–15 K as a function of compressive stress up to 2500 $kg\,cm^{-2}$. Stress was applied using a bellows filled with high-pressure helium gas and measured using a calibrated piezoelectric disc between the sample and mount. The fraction of heat passing along support rods in parallel with the sample was $\lesssim 0.5\%$. Full details of the apparatus will be given elsewhere. The conductivity of an undoped sample GA803 was independent of stress to within experimental error as expected.[6] However, very pronounced effects were seen in three SI samples[6] and a weakly p-type sample GA781 (Fig. 1) where the data are plotted as a function of stress σ in the reduced form $\Delta K/K(0)$, where $\Delta K = K(\sigma) - K(0)$, for three stress directions. Of particular note are the large effects produced by both $\langle 001 \rangle (E)$ and $\langle 111 \rangle (T_2)$ stress con-

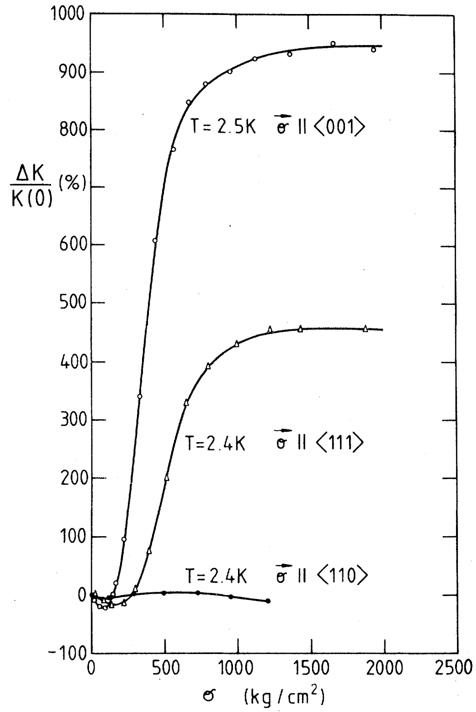

FIG. 1. The stress dependence of the thermal conductivity $\Delta K/K(0)$ of a weakly p-type sample (GA781). We note the strong effects of both $E(\langle 001\rangle)$ and $T_2(\langle 111\rangle)$ stress.

sistent with orthorhombically placed Jahn-Teller wells.[7] The states in these six wells form a representation $^4T_1 + ^4T_2$ whose orbital degeneracy is totally removed by high stress applied in an asymmetrical direction. The overlap between these six orbital states is then very small for strong Jahn-Teller interactions so that there can only be weak phonon scattering from transitions between them and between their two spin doublets. We conclude that Cr^{3+} in GaAs should be a weak scatterer under these conditions. However, as the stress is reduced, the tunneling matrix elements, t, between the wells cause state mixing and strong phonon scattering can now take place because of the existence of phonon matrix elements between components with the same vibrational wave functions; the condition for this for two wells separated by Δ is $\Delta \lesssim t$. In zero stress the tunneling separates the triplets by $4t$ (Ref. 2) and each is spin-orbit split into four levels (Γ_6, Γ_7, and $2\Gamma_8$) giving a total of eight levels. Figure 2 shows how the triplets split, neglecting spin-orbit interaction, under compressive stress applied in the directions used experimentally. The energies were calculated by including the strain matrix elements in the tunneling matrix of Ref. 2. For these symmetry directions some wells remain degenerate so that if they are populated phonon scattering can still occur between them even at the highest stresses provided $t \neq 0$ between these wells.

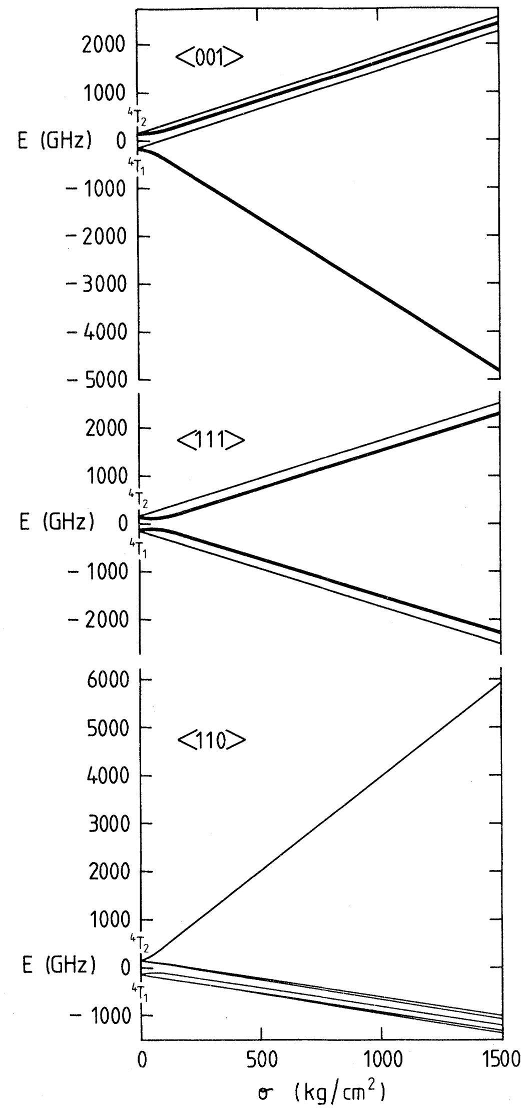

FIG. 2. The energy levels calculated for substitutional Cr^{3+} in GaAs neglecting spin-orbit interaction for $4t = 300$ GHz, $\kappa(E)V_E b = 150\,000$ and $\kappa(T_2)V_T b = 75\,000$ cm^{-1}. The thick lines are doublets.

For high $\langle 001\rangle$ stress ($\Delta >> t$) the scattering within the ground-state orbital doublet and between the doublet and the excited states is quenched so the thermal conductivity should be very close to that of pure GaAs. This can be seen in plots of $K(T)$ at various stress values (Fig. 3). The increase in the conductivity with stress, particularly at low temperatures, is again apparent. The values below 5 K approach those of an n-type Cr-doped sample GA735(064) which shows little or no resonant scattering at these temperatures[4] suggesting that the effect of the scattering at $\sim$150 and 400 GHz, the most important processes at these temperatures, is

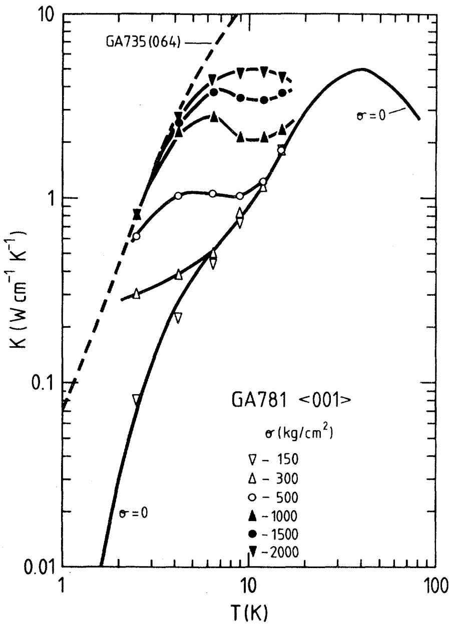

FIG. 3. The thermal conductivity of GA781 at fixed values of stress. The low-temperature data approach those of an *n*-type Cr-doped GaAs sample GA735 (064) showing little or no resonant scattering.

removed by stress of $\sim$1000 kg cm^{-2}. It is interesting though that the effect of the scattering at $\sim$690 GHz becomes more apparent as the low-frequency scattering is removed—a minimum appears at $\sim$9 K—and higher stresses are needed to weaken it. This may indicate a difference in the type of transition although it could reflect effects associated with the increase in reorientation rate due to phonon-assisted processes at these higher temperatures. For strong $\langle 111\rangle$ stress there should only be weak scattering between the two widely separated triplets but strong scattering at $\sim 3t$ within the lower triplet. A very rough indication of its strength relative to that in zero stress can be made by noting that the 27 resonant elastic processes from the ground state in zero stress $[T_1(i)\rightarrow T_2(j)\rightarrow T_1(k)]$ reduce effectively to 2 for high $\langle 111\rangle$ stress.

This seems broadly consistent with the fivefold increase in conductivity observed experimentally (Fig. 1) although we emphasize that the scattering actually takes place between the spin-orbit split levels. $\langle 110\rangle$ stress leaves four closely spaced levels and two singlets, one of which can lie below, within, or above the four depending on V_T/V_E. The last two options seem consistent with the small changes in conductivity seen in Fig. 1. (This sample broke at $\sim$1200 kg cm^{-2} but data for other samples[6] show that these changes remain small up to the highest stresses applied, $\sim$2000 kg cm^{-2}.) We conclude that the behavior observed at high stress is consistent with a dynamic Jahn-Teller model with orthorhombic wells.

As the stress is increased from zero the conductivity first falls to a minimum for all three directions[6] suggesting that a resonant scattering frequency is passing through the maximum in the heat current spectrum. For $\langle 001\rangle$ and $\langle 111\rangle$ stresses this is attributed to the splitting of the T_1 triplet (Fig. 2) with frequencies $\nu_E(\sigma)\sim C_E\sigma$ and $\nu_{T_2}(\sigma)\sim\frac{1}{2}C_{T_2}\sigma$, respectively, where[2]

$$C_E=\left(\frac{1}{\sqrt{2}}\right)\kappa(E)\,V_Eb(s_{11}-s_{12})/h$$

and

$$C_{T_2}=\left(\frac{2\sqrt{2}}{3}\right)\kappa(T_2)\,V_Tbs_{44}/h$$

give the splittings for $t=0$, $s_{11}-s_{12}=1.51\times10^{-11}$, $s_{44}=1.66\times10^{-11}$ m^{2}N^{-1} (Ref. 8); V_E and V_T are defined as in Bates.[9] At temperature T, the minimum occurs at the stress σ_m and frequency ν_m producing a maximum in $W^2(\nu)x^6e^x/(e^x-1)^2$ (Ref. 10) where $x=h\nu/kT$ and $W(\nu)$ is the phonon matrix element. At low temperatures where $\nu_m \ll t$, the calculated values of $W(\nu)$ are approximately constant for $\nu\sim\nu_m$ so that the minimum occurs at $\nu_m\sim 6kT/h$ ($x_m\sim6$), $\sigma_m\propto T$, and V_Eb and V_Tb can be obtained from the slopes. However, as T and so ν_m increase, $W(\nu_m)$ is quenched; the calculated dependence is approximately consistent with $\exp(-0.15\nu_m/t)$. This produces a decrease in x_m and from the temperature range at which this occurs experimentally a rough estimate of t can be found. The data suggest $V_Eb\sim 500\,000\pm250\,000$ and $V_Tb\sim200\,000$ $\pm100\,000$ cm^{-1} [we take $\kappa(E)$ and $\kappa(T_2)$ to have their limiting values of $\frac{1}{4}$ and $\frac{1}{2}$, respectively[7]] and $4t\sim300\pm150$ GHz. Additional information on the coupling constants is provided by the requirement that the four closely spaced levels left by $\langle 110\rangle$ stress should form the ground state (Fig. 2). If this were not the case and a singlet was lowest these four would be rapidly depopulated and the conductivity strongly changed by $\langle 110\rangle$ stress which is not the case experimentally. At high stress, the approximate energies of the four levels and of the other two are $-(\frac{1}{6}/\sqrt{2})K(E)V_Eb(s_{11}-s_{12})\sigma$ and $[(\frac{1}{3}/\sqrt{2})K(E)V_Eb(s_{11}-s_{12})\pm(1/\sqrt{2})K(T)V_Tbs_{44}]\sigma$, respectively.[2,9] Hence the requirement implies $V_T/V_E\lesssim(s_{11}-s_{12})/4s_{44}$ or $V_T/V_E\lesssim\frac{1}{4}$ and modifying our values to comply with this we obtain V_Eb $\sim600\,000\pm300\,000$ and $V_Tb\sim150\,000\pm75\,000$ cm^{-1} which, in fact, bring the lower singlet very close to the four closely spaced levels; Fig. 2. Very-strong-coupling constants have already been inferred from the stress dependence of the EPR[2] and from the very large effects on thermal conductivity $K(T)$ produced by $\sim$1 ppm of Cr^{3+}.[4] The EPR values $V_Eb\sim100\,000$ and $V_Tb\sim35\,000$ cm^{-1} and the mean value from $K(T)$, $Vb\sim150\,000$ cm^{-1}, are substantially lower than the present values which seem improbably large and presumably reflect the very approximate nature of the model used, in particular, the neglect of spin-orbit splitting. If the transition at 690 GHz represents the overall span of the eight levels, $4t \sim 300$ GHz suggests that the spin-orbit splitting of each triplet spans ~ 400 GHz.

It is interesting to compare these data for Cr^{3+} with the negligible effect of stress on an *n*-type sample (GA785) believed to contain a concentration of Cr^{2+} ($^5T_2$) similar to the Cr^{3+} concentration in GA781. In zero stress the conductivity at, say 2 K, is similar to that of undoped GaAs; the only resonant scattering by Cr^{2+} occurs at about the tunneling frequency of $\lesssim 5$ GHz.[4] For the $\langle 110 \rangle$ stresses applied at 2.4 K (dominant phonon frequency $\sim$200 GHz) the splitting of the $^5T_2$ level of up to $\gtrsim 500$ GHz (Ref. 11) passes completely through the heat current spectrum so the absence of any significant change in conductivity suggests that the scattering between these split levels is quenched confirming that for Cr^{2+} the tunneling frequency $\ll 150$ GHz. These very different tunneling frequencies in Cr^{2+} and Cr^{3+} can also reasonably be inferred from the fact that Cr^{2+} gives rise to strong EPR signals[12] and weak phonon scattering[4] implying that most of the ions have strain splittings much greater than the tunneling frequency while exactly the reverse is true for Cr^{3+}.[2,4]

In summary, the sensitivity of the conductivity of Cr-doped GaAs to both $\langle 001 \rangle$ and $\langle 111 \rangle$ stresses confirms that Cr^{3+} has similar coupling to E and T_2 strains. The data are consistent with a model describing slow tunneling between orthorhombic wells with a tunneling splitting $4t \sim 300 \pm 150$ GHz, and the very large coupling constants $V_E b \sim 600\,000 \pm 300\,000$ cm^{-1} and $V_T b \sim 150\,000 \pm 75\,000$ cm^{-1}. We emphasize, however, that spin-orbit splittings were ignored to obtain these estimates.

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[8] From the elastic moduli obtained by R. I. Cottam and G. A. Saunders, J. Phys. C 6, 2105 (1973).

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[10] The change in the conductivity produced by adding a resonant elastic process $\tau^{-1} \tilde{\propto} W^4(\nu_0)\nu_0^2\nu^4/(\nu^2-\nu_0^2)^2$ to frequency-independent scattering $\tilde{\propto} W^2(\nu_0)x_0^6 e^{x_0}/(e^{x_0}-1)^2$ [B. R. Anderson and L. J. Challis, J. Phys. C 8, 1475 (1975)]. In zero stress, the phonon mean free path obtained in Ref. 4 is approximately independent of temperature in this range so this expression should be reasonably applicable.

[11] $\Delta = V_E b(s_{11}-s_{12})\sigma/h\sqrt{2}$ [J. J. Krebs and G. H. Stauss, Phys. Rev. B 20, 795 (1979)] and we take $V_E b \gtrsim 8000$ cm^{-1} obtained in Ref. 4.

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