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Transverse acoustic phonons in germanium near the melting point

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Résumé. — La dispersion des phonons transverses acoustiques du germanium dans les directions [111] et [100] a été étudiée jusqu'à 935 °C, deux degrés seulement au-dessous de la température de fusion T_m . On ne trouve aucun amollissement ni de façon uniforme dans la Zone de Brillouin, ni près du bord de zone. Les énergies des phonons décroissent lentement et linéairement quand T croît de 100 K à T_m . Ceci suggère que la densité électronique à T_m est inférieure à 10^{21} cm^{-3} . Les largeurs de raie des phonons sont très étroites jusqu'à T_m : $\sim 0,035 \pm 0,015 \text{ THz}$, soit des durées de vie $\sim 10 \text{ ps}$ bien que les densités d'électrons libres et de phonons dans le cristal soient élevées près de T_m .

Abstract. — The transverse acoustic phonon dispersion in germanium has been studied along [111] and [100] up to 935 °C, only 2 degrees below the melting point T_m . No evidence of softening is found, neither near the Brillouin Zone boundary, nor uniformly throughout the BZ. The phonon energies decrease slowly and linearly with increasing T from 100 K to T_m . This suggests that the free electron density at T_m is less than 10^{21} cm^{-3} . The phonon linewidths are very narrow up to T_m : $\sim 0.035 \pm 0.015 \text{ THz}$, corresponding to lifetimes of the order of 10 ps, although large densities of phonons and free carriers are present in the crystal near the melting point.

1. Motivation for the study.

Laser annealing of silicon or other semiconductors is a process of great potential technological importance [1]. The primary effect of laser irradiation is the creation of electron-hole pairs, which then can transfer their electronic energy to the lattice. Melting may occur as a conventional, « thermal », process. Several authors, however, have proposed a different mechanism, whereby, under high electronic excitation density, the electron-phonon interaction drives Transverse Acoustic modes to instability [2] before the lattice temperature reaches the usual melting temperature T_m . Such an electronically driven instability leading to melting would be expected to occur for free electron densities of the order of a few 10^{21} cm^{-3} , for atomic density $N \sim 5 \times 10^{22} \text{ cm}^{-3}$.

Recently, Combescot and Bok [3] have calculated that the free electron density in Si should reach a few 10^{21} cm^{-3} at thermal equilibrium near T_m , a much larger density than previously accepted ; hence the possibility that melting of Si, and germanium, could be the result of that new

kind of instability. In support of the possibility that melting of Si and Ge has uncommon features, one may recall that, as is well known, the Lindemann parameters of these substances is smaller than that of common metals [4].

If melting is due to the above mentioned instability, TA mode softening should be observed near T_m . Earlier calculations assumed a uniform softening of the TA modes throughout the Brillouin Zone, proportional to the free electron density n , according to

$$\omega(q, n) = [1 - \alpha n N^{-1}] \omega_0(q) \quad (1)$$

where $\omega_0(q)$ is the dispersion relation in the absence of free carriers i.e. at 0 K, α a proportionality constant and N the atomic density. Using such an assumption, Heine and Van Vechten [5] were able to account quite satisfactorily for the temperature dependence of the energy gap in Si below 400 K. That TA frequencies may become imaginary at large n is illustrated by a former calculation by Martin [6]. Recently, Biswas and Ambegaokar [7], have put forward a theoretical calculation which, to some extent, interpolates between Martin's calculation and the approaches used to describe the phonon dispersion curves of group IV semiconductors in the absence of free electron effects [8]. They do not find a « uniform » softening as in equation (1); instead, softening occurs at the BZ boundary, first at point L , then at point X , for $n \sim 10^{22} \text{ cm}^{-3}$. Again, this could lead to a structural phase transition, for instance melting. Measurement of the TA phonon dispersion near T_m may give information directly relevant to the melting process and, if softening is found, to laser annealing as well.

Ge should behave essentially as Si, for which all the above mentioned calculations were done. Ge was chosen for the present study since it melts at a more accessible temperature $T_m = 937^\circ\text{C}$. Phonons in Ge have been studied extensively [9-13]: the TA mode frequency at point L has been measured up to 430°C , other modes at various points up to 600°C ; these temperatures are too low for anything related to the present problem to be expected, and indeed only a small and general softening of all modes, linear in T , was observed.

2. Experimental setup.

A 3 cm^3 Ge single crystal was mounted with [011] axis vertical between BN plates (in order to avoid any chemical interaction between Ge and its substrate) inside an evacuated furnace able to reach $1\,000^\circ\text{C}$.

The experiments were carried out on the 1T 3-axis spectrometer at the Orphée reactor of LLB, CEN-Saclay, using a Ge (111) monochromator and a pyrolytic graphite (002) analyser, and with horizontal collimations $25'/40'/50'/60'$.

Attention was focussed onto the TA branches along the [111] and [100] directions, with a few measurements taken for comparison on the LA branch. In order to compare with previous results [10-13], some data were taken at 20°C and 600°C . Measurements were then performed at 900, 915 (where the most complete set of data was obtained) 925 and 935°C . During the last run at 935°C the sample partially melted, providing a check of our T -scale ($T_m = 937^\circ\text{C}$).

In order to analyse the data, the variation with temperature and wavevector Q of the intensity scattered outside the phonon peaks was studied and found to be proportional to the wavevector squared and to T therefore corresponding to incoherent inelastic scattering related to the phonon density of states [14]. After subtraction of this intensity, the phonon peaks were fitted to a calculated lineshape, taking into account the known spectrometer resolution function, and assuming a damped harmonic oscillator for the phonon scattering cross-section. Additional assumptions in the fitting were: linear Q -dependence of the dispersion curve, constancy of the dynamical structure factor in the Q region of the fit, neglect of phonon polarization.

3. Results and discussion.

As an example of the data and fit, the neutron groups, measured at 900 °C and 925 °C for the TA phonon at point L — BZ boundary in $[111]$ direction — are shown on figure 1. The solid line is the profile calculated from the 925 °C data with a frequency $\nu = 1.728 \pm 0.002$ THz and linewidth $\Gamma = 0.046 \pm 0.01$ THz. The uncertainty in the frequency determination does not take into account a possible systematic shift which, from the comparison of our data to those published by Nelin and Nilsson [11-13], is less than 0.02 THz.

Fig. 1. — Neutron groups measured at the L_3 point $Q = (3.5, 2.5, 2.5)$ respectively at $T = 900$ °C (+) and $T = 925$ °C (o), with $k_r = 3.5$ Å $^{-1}$. The straight line is the calculated profile for a damped harmonic oscillator with $\omega_q = 1.728 \pm 0.002$ THz and $\Gamma_q = 0.046 \pm 0.010$ THz, fitted to the 925 °C data.

An accurate determination of Γ , which is small in comparison to the instrumental resolution, is difficult to obtain. However, the average of all values obtained by fitting the data at all temperatures from 900 °C to 935 °C is $\Gamma = 0.035 \pm 0.015$ THz. The value found at 600 °C is slightly smaller, in agreement with the observation by Nelin and Nilsson [13], that « the linewidths do not exceed a few units of 0.01 THz anywhere » (between 80 and 880 K). The corresponding lifetime is of the order of 10 ps. Such a value at 900 °C may be evidence of the smallness of anharmonic effects in Ge, even near T_m . It also sets a limit on phonon scattering by electron-phonon interactions, near T_m , that is in presence of electron densities in the range 2×10^{19} to a few 10^{21} cm $^{-3}$ [depending on the theoretical estimates, see Ref. [3] and discussion below].

Figure 2 shows the dependence of TA phonon frequency *versus* temperature, compared to data of reference [13], for points L_3 and X_3 at the BZ boundary, and for point $\left(\frac{1}{4} \frac{1}{4} \frac{1}{4}\right)$ on the lowest TA branch. All frequencies decrease linearly with increasing T up to T_m , at approximately the rate of $(8.5 \pm 0.3) \times 10^{-5}$ K $^{-1}$ found by Nelin and Nilsson [13]. This is particularly clear at L_3 , where softening should occur first according to reference [7]. That the phonon frequencies found here at X_3 are below the linear extrapolation by 0.04 THz might be due to a systematic error. A slight non-linearity in the variation of the frequency at this point cannot be excluded either.

Fig. 2. — Phonon frequencies vs. temperature : a) in the (ξ, ξ, ξ) direction for $\xi = 0.25$ and 0.50 ; b) in the $(\xi, 0, 0)$ direction for $\xi = 1.0$. Circles correspond to the present experiment, triangles to Nelín and Nilsson measurements [13], squares to Brockhouse and Dasannacharya measurements [10]. The straight lines correspond to linear variations $\omega = \omega_0 (1 - KT)$ with K values taken from Nelín and Nilsson, 8.2×10^{-5} in the (ξ, ξ, ξ) direction and 8.6×10^{-5} in the $(\xi, 0, 0)$ direction.

The dispersion of the TA [111] and [100] branches within the BZ has also been investigated. Figure 3 shows the data at 915 °C (the data taken at 920 to 935 °C were identical within our experimental uncertainty, see Fig. 1). Here again, there is no evidence of any softening at the BZ boundary. The arrows indicate the initial slopes of the phonon branches, calculated with $C_{11} = 11.9$, $C_{12} = 4.5$ and $C_{44} = 6.2 \times 10^{11}$ dyn/cm² obtained by linear extrapolation from room- T value [15]. The agreement with experiment near the BZ centre further illustrates that the phonon energy temperature dependence is fairly uniform all along the branch, with a total energy change from 80 K to 1 200 K of $\sim 10\%$.

Finally, neither the temperature dependence of the neutron group integrated intensity, nor the Q -dependence of this intensity along the TA [111] or [100] branches show any anomaly near T_m .

In summary, the study of the dispersion relation of the lowest TA branches in Ge up to its melting point gives no evidence of a softening which might be associated with a high free carrier density, anywhere in the BZ and especially at the BZ boundary. The linear decrease of all phonon energies with increasing temperature, already observed at lower T [13], persists unchanged up to the melting point. It seems therefore that the postulated mechanism of melting *via* the influence of free electrons [2, 3] does not operate in Ge at thermal equilibrium near T_m ; rather, it is over-

Fig. 3. — TA branches in the $(\xi, 0, 0)$ direction (○) and in the (ξ, ξ, ξ) direction (△) at $T = 915^\circ\text{C}$. The initial slopes correspond to $C_{11} = 11.9$, $C_{12} = 4.5$, $C_{44} = 6.2 \times 10^{11}$ dyn/cm². The values found at 925°C are identical to those plotted on the figure.

come by a more common process before the carrier density is large enough. A direct measurement of this density just below T_m would clearly be desirable, and might allow to use the present data in the discussion of laser annealing processes. Equation (1) postulates a variation of $\omega(q)$, linear in n , uniform in q . The variation of $\omega(q)$ found here is uniform in q , but linear in T , of which n depends exponentially. Thus, even at T_m , only a minor fraction of the observed decrease in $\omega(q)$ may be associated to an electronic effect; an upper limit of $n(T_m)$, within the theory of reference [5], can then be calculated : $\omega(T_m)/\omega(R.T) \sim 0.9$, $\alpha = \frac{1}{4} f \epsilon_0 \sim 4$, since $f \sim 1$ and $\epsilon_0 = 16$ neglecting variation of ϵ_0 with T . Therefore $n(T_m) < 10^{21} \text{ cm}^{-3}$, much less than the densities invoked in the plasma melting theory of picosecond laser annealing [2]. 10^{21} cm^{-3} is also the critical density below which no effect of the free carriers on the phonon energies is predicted in (7).

The 10 ps TA phonon lifetime suggested by the observed linewidths indicates that the phonon distribution generated in picosecond laser annealing experiments might be far from thermal equilibrium, and different from that operative when nanosecond pulses are used.

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References

- [1] See for instance, *Laser and electron-beam processing of materials*, ed. by C. W. White and P. S. Peercy (Acad. Press, N.Y.) 1980 ; *Laser and electron-beam solid interactions and materials processing*, ed. by J. F. Gibbons, L. D. Hess and T. W. Sigmon (North Holland, N.Y.) 1981 ; or the recent symposium : « Laser-Solid interaction », *J. Physique Colloq.* **44** (1983) C5.
- [2] See for instance VAN VECHTEN, J. H., *J. Physique Colloq.* **41** (1980) C4-15.
- [3] COMBESCOT, M. and BOK, J., *Phys. Rev. Lett.* **42** (1982) 1413.
- [4] BOK, J., *Phys. Lett. A* **84** (1981) 448.

- [5] HEINE, V. and VAN VECHTEN, J. A., *Phys. Rev. B* **13** (1976) 1622.
 - [6] MARTIN, R. M., *Phys. Rev.* **186** (1969) 871.
 - [7] BISWAS, R. and AMBEGAOKAR, V., *Phys. Rev. B* **26** (1982) 1980.
 - [8] For a recent discussion, see WEBER, W., *Phys. Rev. B* **15** (1977) 4789.
 - [9] BROCKHOUSE, B. N. and IYENGAR, P. K., *Phys. Rev.* **111** (1958) 747.
 - [10] BROCKHOUSE, B. N. and DASANNACHARYA, B. A., *Solid State Commun.* **1** (1963) 205.
 - [11] NILSSON, G. and NELIN, G., *Phys. Rev. B* **3** (1971) 364.
 - [12] NELIN, G. and NILSSON, G., *Phys. Rev. B* **5** (1972) 3151.
 - [13] NELIN, G. and NILSSON, G., *Phys. Rev. B* **10** (1974) 612.
 - [14] MARSHALL, W. and LOVESEY, S. W., *Theory of Thermal Neutron Scattering* (Oxford U. Press) 1971.
 - [15] See for instance, BEILIN, V. M., VELIKOV, Yu. Kh., KADYSHEVICH, A. E. and KRASIL'NIKOV, O. M., *Sov. Phys. Solid. State* **10** (1968) 1226.
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