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LETTER TO THE EDITOR

Effects of isotope disorder on phonons in germanium determined from bound exciton luminescence

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Abstract. The effects of isotope disorder on the energies of the transverse acoustic (TA^L), longitudinal acoustic (LA^L) and transverse optical (TO^L) phonons at the L point have been investigated using the luminescence of excitons bound to copper acceptors. In a sample with approximately equal ^{70}Ge and ^{76}Ge the TO^L phonon is 0.14 ± 0.03 meV higher in energy than expected for a crystal of the same mean atomic mass, while the LA^L phonon is 0.07 ± 0.03 meV lower in energy; the TO^L phonon is also broadened by 0.4 meV. In this disordered sample the Cu no-phonon line is 0.05 ± 0.02 meV higher than expected.

The effects of isotope substitution on the electronic and vibrational properties of germanium have recently been intensively studied. Measurements of the luminescence emitted by electron–hole drops and free excitons [1] and by bound excitons [2] have shown that in single-isotope germanium the lowest indirect electronic energy gap increases with atomic mass number A at the rate $dE/dA = 0.35 \pm 0.02$ meV. This value can be understood in terms of the change in lattice volume with isotope [3] plus the effects of electron–phonon interaction calculated either from first principles [4] or from the temperature dependence of the energy gap [2].

The vibrational quanta change predominantly in proportion to the square root of the atomic mass of the lattice, but in crystals with mixed isotopes the phonon energies are predicted to be also affected by the disorder [5]. For example, the transverse optical phonon at the L point (TO^L) has been predicted to be 0.25 meV lower in energy in a germanium crystal with the naturally occurring mixture of isotopes than in a virtual crystal of the same atomic mass, while the longitudinal acoustic phonon at the L point (LA^L) has been predicted to be unaffected (to within 0.01 meV) by the disorder. Measurements of these phonon energies have been reported using the absorption of infrared radiation when two phonons are created [5, 6]. This process requires the production of phonons of opposite wavevector, so that combinations of modes are observed, with the strength of the absorption being determined partly by the density of two-phonon states. The energy of the TO^L phonon can be measured from its combination with longitudinal optical phonons, but the relevant absorption features are broad and weak [5, 6]. Second-order Raman spectra also provide a way of determining the energy of the TO^L phonon but again the spectra are confused by overlapping features [7].

The energies of the TO^L and LA^L phonons have also been measured from the luminescence emitted by the recombination of the electrons and holes present either as free excitons (FE) or as electron–hole drops (EHD) [1]. At low temperatures, conservation of wavevector requires that recombination of the electron, which has wavevector k_L at the L point, with the hole, located at the Γ point, proceeds with emission of a phonon of wavevector k_L. The phonon energy is given by the difference between the energy of the FE (or EHD) and the energy of the phonon-assisted luminescence feature of interest. However, wavevector conservation forbids no-phonon luminescence from the FE (EHD), so that there is no luminescence signal to characterize the energy of the FE (EHD) itself. It is necessary to estimate this energy in a crystal of the same isotope mixture, introducing a quantity that cannot be directly measured from the luminescence spectrum alone. Recent measurements of the TO^L phonon using this approach were limited to ± 0.3 meV accuracy by the intrinsic linewidth

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of the EHD (3 meV) and by the thermal broadening of the free exciton peaks [1]. No disorder effect was observed for the TO^L phonon in germanium of natural isotopic composition, but the predicted effect of −0.25 meV lies within the uncertainties of the measurement.

The purpose of this Letter is to report experimental measurements of the L point phonon energies in single-isotope and mixed-isotope germanium crystals using luminescence from excitons bound to a shallow acceptor centre. The first advantage of using bound excitons over free excitons is that the binding destroys the kinetic energy of the exciton, and so removes thermal broadening from the linewidth—this broadening amounts to $\sim 1.8kT = 0.65$ meV at 4.2 K. A second advantage is that the spatial localization of the exciton on the centre removes the need for wavevector conservation, allowing both no-phonon and phonon-assisted transitions to be observed. It is then possible to determine the phonon energies directly from the luminescence spectra by taking the difference in energy of the no-phonon line and the phonon-assisted feature of interest. In principle the binding of the exciton to the centre could modify its properties. However, the binding energies are small, ranging, for example, from 1.16 to 1.35 meV for the acceptors Ga, In and Tl [8], compared with a free exciton energy of 740.45 meV (in the limit of low temperature). This binding gives a small enough perturbation to the exciton that the phonon energies determined from the bound exciton spectra are the same as those determined from the free excitons. For example, the LA^L energies derived from the luminescence and absorption spectra for each of Ga, In and Tl are 27.67 ± 0.04 meV [8], compared with 27.72 ± 0.04 meV derived from the free excitons [9] and 27.66 ± 0.03 to 27.70 ± 0.03 meV for the shallow donors Li, Bi, P and As [10]. In this work we have used excitons bound to copper acceptors, which, in contrast to the acceptors Ga, In and Tl, produce easily observable no-phonon luminescence as well as TA^L, LA^L and TO^L phonon-assisted transitions [11]. In germanium of natural composition, we have measured the energy of the LA^L quantum from the Cu spectrum as 27.65 ± 0.03 meV. This value agrees with the values quoted above for shallow acceptors and donors.

The Ge samples used in this work were single crystals with donor and acceptor concentrations typically below 10^{13} cm^{-3}. Copper was either present in the samples or was introduced by scraping them with copper wire and diffusing in at 600 °C for two hours. The luminescence was excited using the 0.5145 μm line of an Ar^+ laser with the samples mounted stress-free and immersed in liquid helium at 4.2 K. It was recorded using a Bomem DA8 Fourier transform spectrometer fitted with a North Coast Ge diode detector cooled to 90 K. The spectral resolution was ~ 0.5–1.0 cm^{-1}.

Figure 1 compares the luminescence from a single-isotope sample (^{76}Ge) with that from a mixed-isotope crystal with 49.4% ^{70}Ge, 2.1% ^{72}Ge, 6.2% ^{74}Ge and 42.3% ^{76}Ge, giving a mean mass number of $\overline{m} = 72.75$. This sample has a large isotopic disorder of $g = 1.6 \times 10^{-3}$ compared with germanium of natural

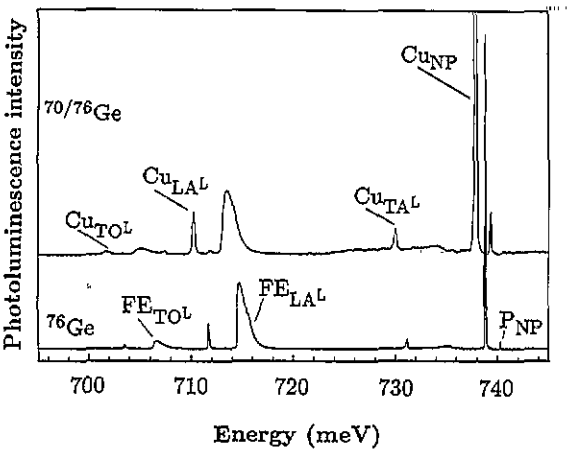

Figure 1. Luminescence at 4.2 K, not corrected for the wavelength dependence of the system, from the decay of free excitons and excitons bound to Cu triple acceptors in a nominally single-isotope sample of ^{76}Ge ($\overline{m} = 75.62$) and the mixed-isotope sample of ^{70}Ge/^{76}Ge with $\overline{m} = 72.75$. Luminescence features labelled are from the free exciton (FE), the Cu acceptor and the P donors. The subscripts indicate the L-point phonons involved in each transition.

isotopic composition for which $g = 5.8 \times 10^{-4}$, where the disorder parameter is defined in terms of the fractional concentration ρ_i of the ith isotope of mass m_i by

$$g = \sum_i \rho_i \left(1 - \frac{m_i}{\overline{m}}\right)^2 .$$

The luminescence in these samples consists of the copper no-phonon line and its TA^L, LA^L and TO^L replicas, plus the TA^L, LA^L and TO^L free-exciton peaks. Note that the TO^L phonon replica is severely broadened in the mixed-isotope crystal compared with the single-isotope crystal.

The energies of the TA^L, LA^L and TO^L phonons have been measured from the differences in energies of the Cu no-phonon lines and the peaks of the phonon sidebands. Figure 2 shows these energies as functions of the mass number for the available crystals. The squares show data from predominantly single-isotope material, and the crosses are for two crystals of mixed isotopes, one with $\overline{m} = 72.75$ and the other a crystal with natural abundances which average to 72.59. The uncertainties in all the data are given by the size of the squares. The lines illustrate the trends expected in the virtual crystal approximation, that is, if the phonon energies varied as the square root of the mean atomic mass of each sample. The lines have been arbitrarily drawn to pass through the data points for ^{74}Ge. The TO^L energy in the mixed-isotope sample with $\overline{m} = 72.75$ is 0.14 ± 0.03 meV higher in energy than expected from the virtual crystal approximation. In contrast, the LA^L energy in the same sample lies 0.07 ± 0.03 meV lower than expected. These opposing effects rule out experimental error caused by a deviation from $\overline{m} = 72.75$ of the part of the sample being used. The consistent deviations in the energies of the TO^L and LA^L phonons reported here and those in figure 5 of [1] exist because in [1]

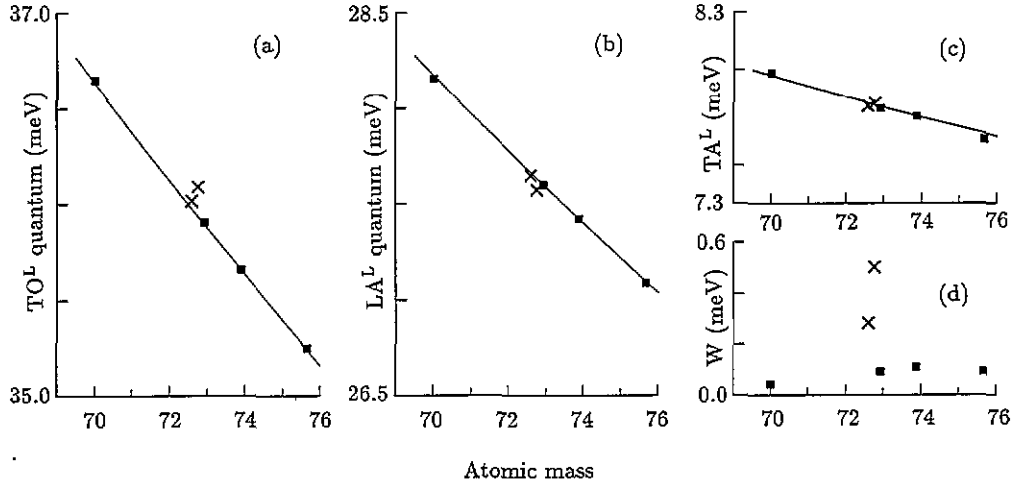

Figure 2. Phonon energies at 4.2 K, derived from the difference in energies of the Cu no-phonon line and the phonon of interest, for (*a*) the TO^L, (*b*) the LA^L and (*c*) the TA^L phonons. The lines show the virtual crystal approximation. The squares are the data for the 'single-isotope' samples and the crosses are for the natural-isotope sample with $\overline{m} = 72.59$ and the mixed-isotope sample with $\overline{m} = 72.75$. The experimental uncertainties in energy for all the samples are given by the heights of the square symbols. In (*d*) are shown the widths W of the TO^L sideband after subtracting the widths of the Cu no-phonon line (observed as an unresolved doublet).

the phonon energies were not derived directly; they were corrected to the values appropriate for 80 K while our data are as measured at 4.2 K. The energy of the TA^L phonon in the mixed crystal with $\overline{m} = 72.75$ is unchanged from the virtual crystal approximation, but since its energy is about four times smaller than the TO^L quantum, a similar percentage change in energy would not be detectable. Luminescence from copper involving the LO^L phonon can just be seen at the limit of detection in our spectra. Any deviation in LO^L energy from the virtual crystal approximation in the mixed-isotope crystals is less than 0.04 meV.

There is a striking effect of the isotope disorder on the widths of the phonon lines. To remove the effects of the finite resolution and inhomogeneous sample broadening, the width of the no-phonon line in each sample has been subtracted from the measured widths of the phonon-assisted lines. For the TO^L peak especially there is a dramatic increase in width in the mixed-isotope samples (figure 2(*d*)) in agreement with the second-order Raman data of Fuchs *et al* [7].

Finally, we consider the energy of the Cu no-phonon line. In the virtual crystal approximation the energy E of the line, which follows the energy of the indirect gap, is expected to differ between two crystals of atomic masses m and m_0 as [1, 2]

$$E = E_0 + C(\sqrt{m/m_0} - 1). \qquad (1)$$

A least-squares fit to the single-isotope data yields $E_0 = 736.71$ meV and $C = 51.67$ meV when the reference mass is taken as $m_0 = 69.92$ as for ^{70}Ge. Subtracting the values of E from the measured no-phonon energies yields the deviations in figure 3. The mixed-isotope sample with $\overline{m} = 72.75$ lies 0.05 ± 0.02 meV higher in energy than the virtual crystal approximation, confirming the need to measure the origin of the phonon energy scale for each isotope composition.

In summary, we have presented data on the effects of isotope disorder on the luminescence from excitons bound to the shallow copper acceptor. We have shown that the transverse optical and longitudinal acoustic phonons at the L point are respectively increased and decreased in energy relative to the virtual crystal approximation, and that the disorder introduces considerable broadening into the TO^L phonon sidebands. The result for the TO^L phonon is of the opposite sign to

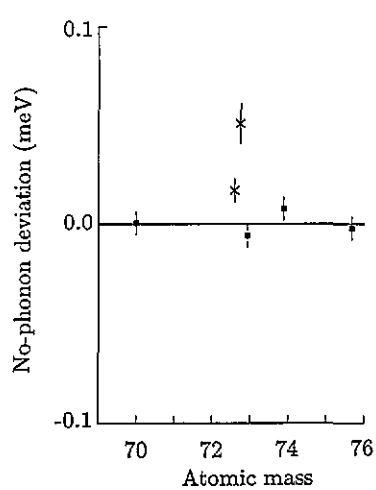

Figure 3. The measured energies of the peak of the Cu no-phonon line at 4.2 K plotted as deviations from the virtual crystal approximation of equation (1). The squares are the data for the 'single-isotope' samples and the crosses are for the natural-isotope sample ($\overline{m} = 72.59$, disorder $g = 5.8 \times 10^{-4}$) and the mixed-isotope sample with $\overline{m} = 72.75$ and $g = 1.6 \times 10^{-3}$.

that predicted and to values derived from two-phonon combination modes [6].

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