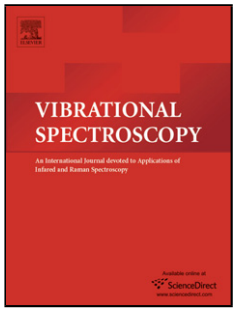

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Measurement of a phonon resonance in a GaSe crystal using THz free induction decay

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Abstract
The relaxation time and absorption and emission profiles of the 0.59 THz TO phonon resonance in a ε-GaSe single crystal were measured using terahertz free induction decay, observed directly as a sequence of decaying sinusoidal oscillations in the time-domain signal following single-cycle pulse excitation. The phonon line profile was also measured using frequency-domain transmission with the resolution of 0.25 GHz and was found to be Lorentzian.

Introduction

Excitation of coherent transients by single-cycle terahertz pulses and observation of their free-induction decay (FID) using time-domain spectroscopy has been demonstrated in a number of molecular gases, and indeed has been employed to study the far-infrared absorption spectra of these gases [1-8]. Molecular gases are particularly suited to this type of study, because they possess very narrow absorption lines and negligible (or low) absorption at other frequencies; moreover the gases studied have been linear molecules with regularly spaced resonance lines. Although the process of excitation and subsequent free induction decay of coherent transients can also take place in solids possessing resonances at appropriate frequencies, its observation is usually hampered by the presence of multiple excitations at irregular frequencies, short relaxation lifetimes, and by other types of transmission loss.

Here we report observation of free-induction decay in a nonlinear ε-GaSe crystal where it is due to the phonon mode at 0.59 THz. It is well established that layered GaSe crystals grown by the Bridgman method possess ε-polytype structure, where the primitive cell belongs to the $\bar{6}m2$ point group symmetry and includes two layers, each containing four (Se-Ga-Ga-Se) monoatomic layers. The forces between layers are weak van der Waals bonds, whereas the intralayer forces are the much stronger ionic-covalent bonds. As a result, ε-GaSe exhibits a strongly pronounced structural anisotropy, with a quasi-two-dimensional character where interlayer coupling has only a weak effect on the vibrational frequencies of the lattice modes. The phonon mode examined in this study is the TO (transverse optical) rigid interlayer phonon mode $E'^{(2)}$ at 0.59 THz [9], which is an intense resonance with a narrow linewidth.

A high-purity, highly homogeneous *z*-cut GaSe crystal of a single ε-polytype and with a low concentration of defects is a very good solid medium for observing excitation and decay of coherent transients, due to two crucial advantages. First, in the measurement frequency range of 0.2-3 THz there is only a single intense phonon resonance at 0.59 THz with a particularly narrow linewidth. Moreover, this resonance lies sufficiently far in frequency from other TO phonons and plasma frequency that the "background" absorption loss is low (see Fig. 1).

However, the quality of the GaSe crystal is crucially important. Grown GaSe crystals may have variable amounts of stacking faults and micro- and point defects, and can contain a mixture of four possible polytypes, all arising from the growth technology that can produce increased interlayer bonding. Such GaSe crystals – i.e., which are astoichiometric and possess high concentrations of micro-defects or interlayer intercalated impurity atoms – have low optical quality, easily seen upon careful, sometimes even visual, examination. As a result, vibrational spectra of these crystals present combinations of LO (longitudinal optical) with acoustic phonons, or Raman-active but IR inactive phonon modes. Particular examples observed in low quality GaSe include absorption peaks attributed to difference frequency combinations of acoustical and optical phonons: $A_2''(TO) - E''$ at 0.80 THz (26.7 cm^{-1}), $E'(LO) - E''$ at 1.24 THz (41.3 cm^{-1}), $A_1' - E'(LO)$ at 1.57 THz (52.3 cm^{-1}), and $A_1' - A_2''(LO)$ at