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Raman Scattering in Gray Tin[†]

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The first-order one-phonon Raman spectrum of gray tin (α-Sn) and its temperature dependence is reported. The results are compared with recent work on germanium and silicon.

The first-order one-phonon Raman spectrum of germanium and silicon has been reported by Parker *et al.*[1] at room temperature. Hart *et al.*[2] have recently observed the temperature dependence of the one-phonon Raman line of silicon. We report here the observation of one-phonon Raman scattering in gray tin. From these observations, the Raman frequency of gray tin (optical phonon frequency at $\vec{q} = 0$) and its temperature dependence have been determined.

Our measurements were performed on (111) surfaces of growth of single crystals, grown from the mercury solution.[3] Measurements were also performed on polycrystalline materials prepared by keeping high-purity white tin, seeded with InSb, in the freezer compartment of a refrigerator for several days. The measurements on the single crystals were performed at 77 °K, with the sample immersed in liquid nitrogen, and at 0 °C: Measurements at higher temperatures are not possible since existing pockets of mercury diffuse through the crystal and destroy it above 0 °C. The polycrystalline samples were measured at room temperature without any visible transformation into white tin.

The back-scattering measurements were made with the 4879.9-Å line of a $\frac{1}{2}$-W argon-ion laser (Coherent Radiation Model 54). A Jarrell-Ash 1-m double monochromator, with detection by photon counting, was used. The wavelength of the phonon-shifted line was determined by comparison with the 4928.2-Å line of a low-pressure neon lamp. The scattering surface was nearly parallel to the entrance slit while the laser beam was kept at an angle of 30° with the normal to that surface. In the experiment with the single crystal, the selection rules were checked to be those corresponding to the $\Gamma_{25'}$ phonons and the (111) surface.

The phonon-shifted Raman spectra of the single-crystal sample at 77 °K and that of the polycrystalline sample at 297 °K are shown in Fig. 1. We observe that the optical phonon frequency obtained at 77 °K [$\nu_0(77\,°\text{K}) = (5.973 \pm 0.03) \times 10^{12}$ Hz] is in excellent agreement with the result of neutron scattering experiments [$\nu_0(77\,°\text{K}) = (6.00 \pm 0.06) \times 10^{12}$ Hz].[4]

It has recently been suggested by Martin[5] that the restoring forces of materials of a given family,

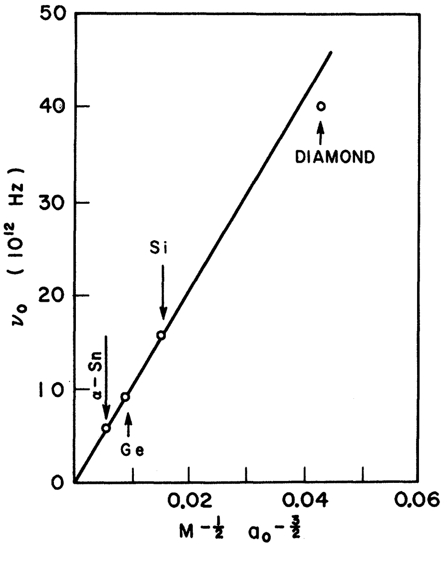

FIG. 1. One-phonon Raman spectrum of polycrystalline α-Sn at 297 °K and of single-crystal α-Sn at 77 °K.

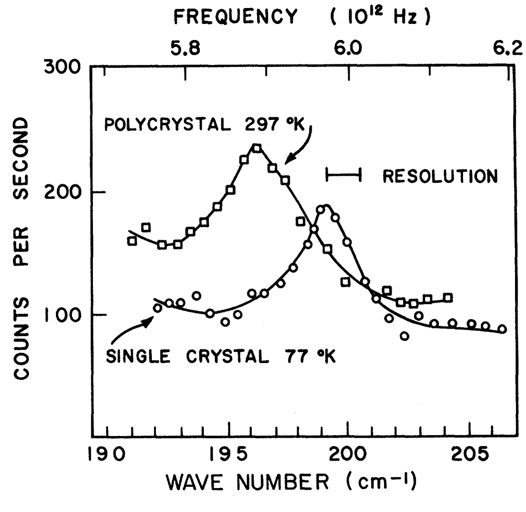

FIG. 2. Raman frequencies of diamond, Ge, Si, and α-Sn as a function of $M^{-1/2}\ a_0^{-3/2}$. (M is the atomic mass in amu, a_0 the lattice constant in Å.)

mostly of electrostatic origin, should scale like the inverse third power of the lattice constant a_0. This should yield a Raman frequency ν_0 proportional to $a_0^{-3/2}M^{-1/2}$ for the materials of the germanium family (M is the atomic mass). We have plotted in Fig. 2 the room-temperature values of ν_0 as a function of $a_0^{-3/2}M^{-1/2}$ for Si, Ge, and α-Sn[6]: The proportionality mentioned above is well satisfied. The Raman frequency of diamond[7] falls 10% below the line of Fig. 2. The simple-bond-charge model[8] predicts the following relationship between ν_0 and the bulk modulus B:

$$B = M(\pi\nu_0)^2/2a_0 \quad . \tag{1}$$

The value of B calculated with Fig. 1, $B_{\text{calc}} = 5.4 \times 10^{11}\,\text{dyn}\,\text{cm}^{-2}$, is in good agreement with that determined by Price and Rowe [$B_{\text{exp}} = (5.3 \pm 1) \times 10^{11}\,\text{dyn}\,\text{cm}^{-2}$] from the neutron-diffraction data for acoustical phonons.[4]

The Raman frequency of the single crystal at 273 °K [$\nu_0(273\,°\text{K}) = (5.897 \pm 0.03) \times 10^{12}\,\text{Hz}$] agrees well with that found for the polycrystalline sample at a slightly higher temperature [$\nu_0(297\,°\text{K}) = (5.885 \pm 0.03) \times 10^{12}\,\text{Hz}$]. The shift in ν_0 between 77 °K and room temperature is

$$\nu_0(77\,°\text{K}) - \nu_0(297\,°\text{K}) = (8.8 \pm 3) \times 10^{10}\,\text{Hz} \ ,$$

comparable to that observed by Hart *et al.*[2] for Si in the same temperature range.

It is interesting to note that when hydrostatic pressure is applied to diamond,[9] Si,[10] or Ge,[11] ν_0 does not vary like a_0^{-2} but rather like a_0^{-3}. This stronger lattice-constant dependence is undoubtedly due to hard-core effects: The lattice becomes stiffer if one changes a_0 by compression than if one reduces a_0 by going from one material to another, thus reducing at the same time the atomic size. The observed temperature shift of ν_0, both for Si[2] and for α-Sn, is about four times larger than that naively predicted from the change of a_0 due to the thermal expansion.

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Electron Tunneling into $KTaO_3$ Schottky Barrier Junctions

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Electron tunneling techniques have been used to examine the characteristics of current (I) vs voltage (V) in degenerate n-type $KTaO_3$ Schottky barriers at 1 °K. The d^2V/dI^2-vs-V curve exhibits structure at each of the four LO modes in $KTaO_3$: 22.5, 34, 51.5, and 102.5 mV. Several two-phonon peaks were also seen and identified as $51.5 + 102.5 = 154$-mV and $2 \times 102.5 = 205$-mV combinations. The almost antisymmetric nature of the phonon-induced structure about zero bias indicates that it is caused by the inelastic interaction of the tunneling electrons with phonons in the barrier. In addition, the maximum in the differential resistance dV/dI occurs at a bias equal to the Fermi level of the semiconductor, and an effective conduction-band mass $m^* = 0.5m_0$ of the free carriers has been determined.

I. INTRODUCTION

It is now well established that electron tunneling can be a primary mechanism for current transport in metal-semiconductor (MS) Schottky barriers.[1,2] In an n-type degenerate semiconductor, such as $KTaO_3$ used in this work, the barrier is characterized by a negative surface-charge density fol-