Raman Scattering Measurements of the E_g Optical Phonon in V_3Si

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We report Raman scattering measurements on the E_g (Γ_{12}^+) optical phonon measured from 50–340 K on a single crystal of V_3Si. This phonon line has an anomalous width, shape, and temperature dependence, suggesting direct coupling between the phonon and electronic excitations.

We present Raman measurements on V_3Si, the first measurement on an intermetallic compound with the $A15$ structure. These materials are remarkable both for their high-temperature superconductivity ($T_c \approx 17$ K for V_3Si) but also for the nearly complete softening of the $C' = \frac{1}{2}(C_{11} - C_{12})$ elastic constant that sometimes terminates in a martensitic transformation somewhat above T_c.[1,2] The corresponding zero-wave-vector strain has E_g (Γ_{12}^+) symmetry and should couple bilinearly with a zero-wave-vector optical phonon of the same symmetry. A harmonic-lattice-dynamical calculation by Sham yielded a softening of only C' and of the E_g phonon through d-electron–lattice coupling. No other modes were affected.[3] Later theories of the martensitic transformation assumed an electronic instability of the Jahn-Teller type (Labbé and Friedel[4]) that couples directly to the strain and hence indirectly to the phonon or of a pseudo-Peierls type (Gor'kov[5] and Bhatt and McMillan[6]) that couples directly to the phonon and hence indirectly to the strain. Bhatt has recently analyzed Landau theories of both types of coupling,[7] and has found that they take a common phenomenological form with one exception—direct coupling to the strain by itself should not produce a softening of the phonon with decreasing temperature. We have studied this phonon by Raman scattering and present evidence of a small amount of softening, thus suggesting that some direct electronic coupling to the sublattice distortion (phonon) must be present. Beyond that, our data show a strongly temperature-dependent, asymmetric line shape—additional evidence of strong electron-phonon coupling.

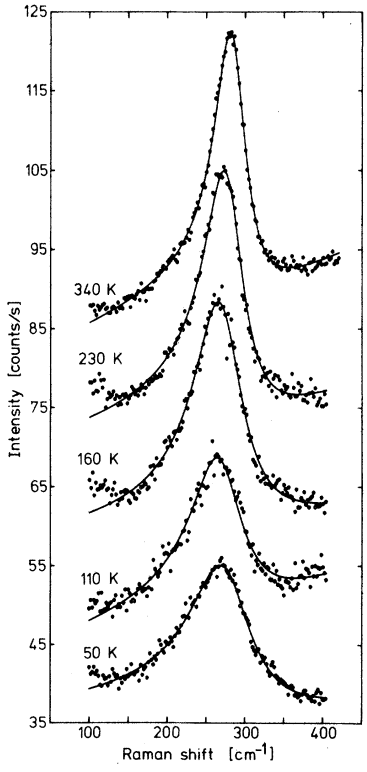

FIG. 1. The E_g spectrum at five temperatures, taken with a [(100),(100)] polarization geometry (Ref. 8). Quoted temperatures represent measured values plus 30 K. The spectra are shifted upwards by 55 counts/s (340 K), 40 counts/s (230 K), 25 counts/s (160 K), and 10 counts/s (110 K). The dwell time was 60 s, with exception of the 50-K and 340-K spectra when it was 120 s. Lines represent fits to Eqs. 1(a) and 1(b): Lorentzian with antiresonance.

Our main results are shown in Fig. 1, which presents Raman spectra at various temperatures taken with a [(100), (100)] polarization geometry (A_{1g} plus E_g spectra). Other measurements with a polarization geometry that produces only E_g spectra have proven that the peak at 280 cm^{-1} (34.7 meV) has E_g symmetry. It has three unusual properties: temperature dependence of peak position and of line width, and asymmetric shape. Its frequency seems to decrease slightly with decreasing temperature. Phonon softening has previously been observed in the phonon density of states of V_3Si as measured by inelastic neutron scattering. It was particularly pronounced below 20 meV but also apparent near 33 meV.[8] This softening is not expected for a phonon whose self-energy is dominated by anharmonic interactions. We conclude, following Bhatt,[7] that softening of the Raman line is evidence for some direct coupling between an incipiently unstable electronic charge distribution and E_g phonons.

More striking is the temperature dependence of the width, which doubles as T decreases from 340 to 50 K. Such an increase is not possible with the usual anharmonic processes and is additional evidence for electronic interactions. The peak is asymmetric, being narrower on the high-energy side. This high-energy falloff is probably caused by a Breit-Wigner-Fano interference between a sharp line and a continuum. The solid lines in Fig. 1 are fits to an expression that results from a coupled-mode theory, namely,

$$S(\omega) = \frac{\hbar\pi^{-1}(1-e^{-\beta\omega})^{-1}2\Gamma\omega\alpha_c^2 f(\omega)}{(\omega_0^2-\omega^2)^2+4\Gamma^2\omega^2}, \quad (1a)$$

$$f(\omega) = (\omega_a^2-\omega^2)^2/\lambda^2, \quad (1b)$$

with parameters given in Table I. Here $\beta=\hbar/k_B T$; ω_0 is the renormalized phonon frequency; Γ is its width; and ω_a is the antiresonance frequency. The fitting procedure superposed Eq. (1) on a linear background, and weighted the peak region about 15 times more heavily than the wings. Fits to the usual Lorentzian, i.e., Eq. (1a) with the antiresonance factor $f(\omega)$ set equal to unity, did not reproduce the asymmetric line shape very well; their values for χ^2 were almost twice as large as fits using $f(\omega)$ given by Eq. (1b). Because ω_a is many linewidths above ω_0, the values of ω_a in Table I are not very precise. More reliable are the temperature dependences of ω_0 and Γ_0.

TABLE I. Fitting parameters (cm^{-1}).

Temp. (K)	ω_0	Γ	ω_a
340	286.0	24.2	400
230	280.2	30.8	405
160	273.8	37.8	459
110	273.7	39.8	426
50	281.8	47.2	447

We have looked for other Raman lines and have found neither the T_{2g} (Γ_{25}^+) Raman-active mode (not expected to show softening[3]) nor the inactive $\Gamma_{15}^{(-)}$ and $\Gamma_{25}^{(-)}$ modes once predicted to show softening.[9] (In principle, the latter might be rendered weakly Raman active by surface-induced parity mixing.[10])

Some details of the experimental technique will now be given. A crystal of V_3Si was grown from buttons of stoichiometric arc-melted starting material by the Czochralski technique in a tri-arc furnace using a water-cooled hearth in 1 atm of argon. The conducting properties of the seed end of the boule were $T_c = 16.86$ K, width of $T_c = 0.31$ K, and resistance ratio = 12.5; at the other end, $T_c = 16.84$ K, $\Delta T_c = 0.03$ K, and ratio = 17.5 K. The Raman sample was from an intermediate position. A [100] surface was spark cut, mechanically polished with alumina, and then electropolished using an aluminum electrode in a solution of two parts of 85% lactic acid and one part each of 48% HF, 70% HNO_3, and 95% H_2SO_4 for 4 min at 6 V. Laser light of 514-nm wavelength was incident at a pseudo-Brewster angle of about 70°; the 0.4-W beam formed an 0.15×0.05-mm^2 illuminated area. The scattered light was collected in a direction normal to the surface and focused onto the entrance slit of a 0.75-m Spex monochromator equipped with a third monochromator. The resolution was 9 cm^{-1}.

Temperatures quoted here represent values measured with a thermocouple plus 30 K. This is close to the upper limit of the calculated temperature rise caused by the laser beam. Cooling was provided by flowing cold helium gas in a modified "Heli-Tran" system.

The most striking feature of Fig. 1 is the broadening. The asymmetry is less well established, but we believe it to be real. If so, it could either result from an interference, as in Eq. (1), or from an unusual frequency dependence of the phonon self-energy. In the latter case Eq. (1) would apply but with $f=1$, and either ω_0^2 or

Γ, or both, would vary with frequency; one can show that they must be even functions of ω.

An interference of the type described by Eq. (1) has been seen between the Raman-active phonon and intervalence band Raman-active electronic excitations in heavily doped p-type Si.[11] Theoretical explanations have been either phenomenological[11] or based upon microscopic calculations.[12] We suggest that the asymmetry in V_3Si, if real, has a similar origin to that in p-Si. The following conditions can be shown to lead to Eq. (1): (1) First-order Raman coupling to a phonon; (2) Raman coupling to an excitation operator for a continuum whose response function R (Fourier transform of the retarded Green's function) has an imaginary part proportional to frequency; and (3) linear coupling [via the parameter λ in Eq. (1b)] of the phonon coordinate to the excitation operator for the continuum. Then one obtains the phonon self-energy parameters

$$\Gamma = (\lambda^2/2\omega)\,\mathrm{Im}R(\omega), \tag{2a}$$

$$\omega_0^2 = \omega_Q^2 - \lambda^2\,\mathrm{Re}R(\omega), \tag{2b}$$

and the antiresonance frequency

$$\omega_a^2 = \omega_Q^2 + \lambda\alpha_Q/\alpha_c, \tag{2c}$$

where ω_Q is the bare phonon frequency and where α_Q and α_c are amplitudes for Raman coupling to the phonon and to the continuum.

It is possible that the Fermi energy in V_3Si cuts the uppermost filled energy bands near points of degeneracy in the Brillouin zone. Gor'kov[5] and Lee and Birman[13] have discussed some examples. Then vertical transitions among such bands could produce such a continuum, as in p-Si. Some of the degeneracy would be removed by sublattice distortion of E_g symmetry, giving strong, direct electron-phonon coupling.

To summarize, we have observed the E_g (Γ_{12}^+) optical phonon for the first time in any $A15$ compound. Its width grows markedly with decreasing temperature, and there is some softening. Both effects are evidence of a strong electron-phonon interaction. The Raman line shape is slightly asymmetric, suggesting an antiresonance between Raman coupling to the phonon and to interband electronic excitations.

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