RAMAN SCATTERING IN V$_3$Si, V$_3$Ge, Nb$_3$Sb, AND Cr$_3$Si : CORRELATION OF E$_{g}$ OPTICAL PHONON LINEWIDTH WITH MAGNETIC SUSCEPTIBILITY


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Abstract.- Raman scattering measurements of the E$_g$ optical phonon in V$_3$Si and Nb$_3$Sb show it to have an anomalous width, temperature dependence, and asymmetric lineshape. We have observed a similar, although weaker, anomaly in V$_3$Ge. The E$_g$ and T$_a$ phonons in Nb$_3$Sb and the T$_a$ phonon in Cr$_3$Si show no anomalous behavior and can be understood in terms of simple anharmonic interactions. In Cr$_3$Si the E$_g$ phonon has an anomalous width, shape, and temperature dependence (similar to V$_3$Ge) in spite of its low electronic density of states and temperature independent magnetic susceptibility. A linear correlation is shown to exist between magnetic susceptibility and E$_g$ mode linewidth, $\Gamma$, in V$_3$Si, Nb$_3$Sb, and V$_3$Ge. With the aid of a simple model, most of the features of the Raman data can be understood in terms of direct coupling of the E$_g$ phonon to interband electronic transitions between the very flat bands originating from the T$_a$ level in these compounds. These results indicate that direct coupling of the E$_g$ optical phonon to the T$_a$ bands plays a major role in the splitting of the $\Gamma_{15}$ subband $\tilde{N}$(E) peak by the dimerization of the transition metal sublattice.

1. Experiment.- A single crystal of V$_3$Ge ($T_c=6.3K$) was grown from buttons of stoichiometric arc-melted starting material by the Czochralski technique.$^1$ The single crystal of Cr$_3$Si ($T_c=0.015K$) was grown by zone refining pressed stoichiometric powder mixtures of Chromium and Silicon.$^2$ (100) surfaces were spark cut from these samples and then mechanically polished with alumina. For the investigation on Nb$_3$Sb, a large single crystal was grown by closed tube vapor transport with iodine as a transporting agent. The Raman measurements were performed on a high quality, smooth, as-grown (110) face of the crystal. Laser light of 514-nm wavelength was incident at a pseudo-Drewster angle of 70$^\circ$, collected in a direction normal to the surface, and analyzed with a home-built double monochromator employing standard photon counting electronics. Cooling was provided by either flowing cold He gas in a modified "Hell-Tran" system or a liquid He Janis cryostat. True sample temperatures were determined from Anti-Stokes/Stokes ratios of the E$_g$ phonon.

2. Results and Discussion.- The E$_g$ symmetry Raman spectra of V$_3$Ge taken at 340K and 50K are shown in Fig. 1. The phonon frequency hardens from 278 to 287, cm$^{-1}$ and the linewidth increases from 37.2 to 69.5 cm$^{-1}$ (FWHM) upon cooling. The solid lines are fits to a spectral function resulting from a coupled-mode theory, wherein the asymmetric lineshape is due to a Breit-Wigner-Fano interference between the discrete phonon and an electronic continuum.$^3$
We propose that the dominant damping mechanism for the $E_g$ mode in this $A$-15 and in $V_3Si$, $Nb_3Sn$, and $Cr_3Si$ consists of inter-band processes wherein the $E_g$ mode decays into electron-hole pairs in the $\Gamma_{12}$ bands. These bands are within an energy comparable to the $E_g$ phonon energy of the Fermi level throughout large regions of the Brillouin Zone.\(^5\) Due to symmetry based selection rules, the $T_{2g}$ phonon in $Nb_3Sn$ cannot interact with these bands and it has indeed been observed to be relatively weakly damped.\(^6\)

In $Nb_3Sb$ and $Cr_3Si$ the $E_g$ phonon cannot interact with electrons in the $\Gamma_{12}$ bands since they are ~0.35 eV below the Fermi level and hence completely filled. Accordingly, the $E_g$ phonon in $Nb_3Sb$ and the $T_{2g}$ phonons in both $Nb_3Sb$ and $Cr_3Si$ are weakly damped and harden and narrow upon cooling. This is typical behavior for phonons whose self-energy is dominated by anharmonic phonon-phonon interactions.

The $E_g$ phonon in $Cr_3Si$ is not so well understood. It appears to harden from 310. to 320. cm\(^{-1}\) and broaden from 40. to 60. cm\(^{-1}\) upon cooling from 300K to 70K. However, additional structure in the region of the phonon, possibly due to electronic Raman scattering, complicates the analysis.

The electronic nature of the $E_g$ phonon damping in $V_3Si$, $Nb_3Sn$, and $V_3Ge$ is further demonstrated by plotting their magnetic susceptibility, $\chi$, versus their corresponding $E_g$ mode linewidth at the same temperature, for several temperatures. This is shown in Fig. 2 for the temperature range 400K to 20K, where a strong correlation is seen to exist, with the $V$-based compounds following one relationship and $Nb_3Sn$ a separate one. Such a division of $V$-based and $Nb$-based $A$-15 compounds into two families, with $\eta_{Nb_3Sn} = \eta_{V_3Si}$, where $\eta = N(E_F)\langle I^2 \rangle$, $\langle I^2 \rangle$ being the Fermi surface averaged electron-phonon matrix element squared, has already been pointed out by Klein, et. al.\(^8\) The ratio of the initial slopes of the two curves (indicated by the solid lines through the data in Fig. 2) is in good agreement with the ratio of $\langle I^2 \rangle_{Nb_3Sn}/\langle I^2 \rangle_{V_3Si}$ as calculated by Klein, et. al.\(^8\) The temperature dependence of the magnetic susceptibility is commonly ascribed to thermal repopulation of electronic energy levels near a sharp peak in the electronic density of states. The strong correlation between the magnetic susceptibility and the $E_g$ phonon linewidth, shown in Fig. 2, suggests that electron-phonon interactions (as opposed to anharmonic phonon-phonon interactions), subject to the same thermal repopulation effects as the magnetic susceptibility, are responsible for the temperature dependence of
the $E_g$ phonon linewidth and frequency in these compounds. Indeed, a simple model of the interaction and the $\Gamma_{12}$ bands is able to account quantitatively for the linewidth temperature dependence. Our model will be discussed more fully in a future publication. These results are in accord with the recent conclusions of Mattheiss and Weber\cite{11} that dimerization of the transition metal sublattice is the primary driving mechanism for the martensitic transition.

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![Graph showing correlation of $\chi$ vs. $\Gamma$ for V$_3$Si, Nb$_3$Sn, and V$_3$Ge.](image)

Fig. 2: Correlation of $\chi$ vs. $\Gamma$ for V$_3$Si, Nb$_3$Sn, and V$_3$Ge. Raman data for Nb$_3$Sn taken from ref. 4, data for V$_3$Si, V$_3$Ge, and Nb$_3$Sn taken from refs. 9, 9, and 10, respectively.

References