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Raman studies of *A*15 compounds

S. Schicktanz, R. Kaiser, E. Schneider, and W. Gläser
*Physik Department der Technischen Universität München,
München, Federal Republic of Germany*

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The Raman spectra of transforming and nontransforming V_3Si crystals and of nontransforming Nb_3Sn were measured between 400 and 20 K. For transforming V_3Si the frequency of the E_g Raman peak decreases down to 120 K, but increases below this temperature. On the other hand, the width of the peak increases down to 90 K, but decreases at lower temperatures. No frequency increase and no decrease in width at low temperatures is found for the nontransforming V_3Si sample. For Nb_3Sn the peak frequency increases only little at low temperatures. These phenomena are interpreted as resulting from two Raman peaks, the first deriving from the cubic, the second from the tetragonal lattice structure. At $T > T_m$ (martensitic transition) the existence of the second peak is believed to indicate the presence of tetragonal domains. These domains are thought to be present in the transforming V_3Si sample even at temperatures above 100 K. Practically no or little tendency for forming tetragonal structure is found in the nontransforming V_3Si and Nb_3Sn samples, respectively. The surface versus bulk question is discussed.

I. INTRODUCTION

Recently, the first Raman spectra of a transition metal compound with *A*15 structure have been measured.[1,2] The two independent investigations centered on different aspects. In the study done in our laboratory[1] the very weak defect induced Raman spectrum of V_3Si was found in satisfactory agreement with the phonon density of states determined by neutron scattering. In the other work on V_3Si by Wipf *et al.*[2] the intense allowed Raman line of E_g symmetry was shown to shift to lower frequency and increase in width with decreasing temperature. The lowest temperature reached in this work was 50 K.

Since the E_g mode of V_3Si is coupled to the tetragonal distortion[3,4] it seemed interesting to investigate how this mode behaves in the neighborhood of the temperature ($T_m \sim 20$ K) where the transition from a cubic lattice ($T > T_m$) to a tetragonal structure ($T < T_m$) occurs.[5] Raman investigations at such low temperatures are difficult to perform because the impinging light may increase the temperature of the illuminated spot considerably.[1,6(a)]

Next to V_3Si the other most thoroughly studied *A*15 compound is Nb_3Sn. Both materials are superconducting with high values of T_c (16–18 K). Therefore, we have extended our Raman studies to Nb_3Sn. The Raman spectrum of Nb_3Sn will be compared with the phonon density of states obtained from neutron data and the temperature dependence of the E_g mode will be investigated down to a temperature of ~20 K.

II. SAMPLES AND EXPERIMENTAL

A. V_3Si samples

The two V_3Si samples (a) and (b), the same as in our previous study,[1] were cut from single crystals of V_3Si grown by the floating zone technique. X-ray diffraction at low temperatures shows that sample (a) has a cubic to tetragonal transformation at ~22 K. This sample is taken as stoichiometric (25 at.% Si). The superconducting transition temperature T_c is 16.9 K and the resistance ratio $\rho = R_{300\,K}/R_{18\,K} = 36$. In contrast to sample (a) no transformation could be found in sample (b). Sample (b) has a Si content 0.9 at.% less than sample (a) according to electron probe analysis (relative accuracy 0.1 at.%). From the reference sample (a) the concentration of 24.1 at.% Si follows for sample (b). This sample has a T_c of 16.2 K and a resistance ratio $\rho = 11.3$.

B. Nb_3Sn sample

The Nb_3Sn sample supplied to us was produced by chemical vapor deposition. The sample contains large crystallites. It follows from x-ray measurements that our Nb_3Sn sample is not transforming (Nb_3Sn: $T_m \sim 40$ K). X-ray fluorescence analysis gives a concentration of 24.5 ± 0.5 at.% Sn. The superconducting transition temperature T_c is 18 K.

C. Experimental

The Raman scattering was measured with standard equipment. The experiments were performed with a spectral resolution of about 7 cm^{-1} in three geometries in which the Raman modes of $A_{1g}(\Gamma_1)$, $E_g(\Gamma_{12})$, $F_{2g}(\Gamma'_{25})$ can be obtained. The laser intensities varied from 20 to 500 mW. Correspondingly, the dwell time per point was from 160 to 40 s (several runs added). In order to avoid a significant increase in temperature of the spot illuminated by the incident light, for the low-temperature measurements laser intensities as low as 20 mW were used. At temperatures above 100 K the temperature of the illuminated spot was obtained from the ratio of the Stokes and anti-Stokes Raman intensities. With the sample holder at liquid nitrogen temperature the increase ΔT at the illuminated spot was determined for various laser intensities (20–500 mW). The same ΔT was assumed to occur (no measurable anti-Stokes Raman intensities exist at $T < 100$ K) when the sample holder was at 4.2 K since the heat transfer from the illuminated spot to the coolant is not strongly temperature dependent. The estimated uncertainty in temperature is given by a horizontal bar for each measurement in Figs. 2 and 4. Correspondingly, the vertical bars give the uncertainty in peak frequency and width, respectively. The Raman scattering was measured on unpolished surfaces of fracture thereby excluding any perturbation by the polishing process.

III. RESULTS

A. V_3Si

Some of the E_g Raman spectra measured at different temperatures for the transforming V_3Si sample (25.0 at.% Si) and the nontransforming sample (24.1 at.% Si) are presented in Figs. 1(a) and 1(b). The structure on the left wing of the bands in Fig. 1(b) is due to defect induced Raman scattering.[1] The temperature dependence of the peak frequency and width for the allowed scattering are given in Figs. 2(a) and 2(b). It follows from Fig. 2(a) that the peak position of transforming V_3Si shifts to lower frequencies when the temperature decreases from several hundred degrees to ~ 120 K. At ~ 120 K the trend reverses and the peak frequency increases when the temperature is lowered. Though only the softening of the E_g mode is mentioned in Ref. 2, there the 50 K peak lies a few cm^{-1} above the 110 K value.

The softening of the E_g mode from 400 to ~ 120 K amounts to 9% of the 400 K value, the peak frequency increases from ~ 120 to ~ 30 K by 7% of the 120 K value. For the nontransforming crystal the softening of the E_g mode between 400 and ~ 120 K is weaker than for the transforming sample. From ~ 120 down to ~ 20 K the E_g frequency of this sample remains practically constant.

Similar to the peak position for the transforming V_3Si sample the width of the E_g vibration band

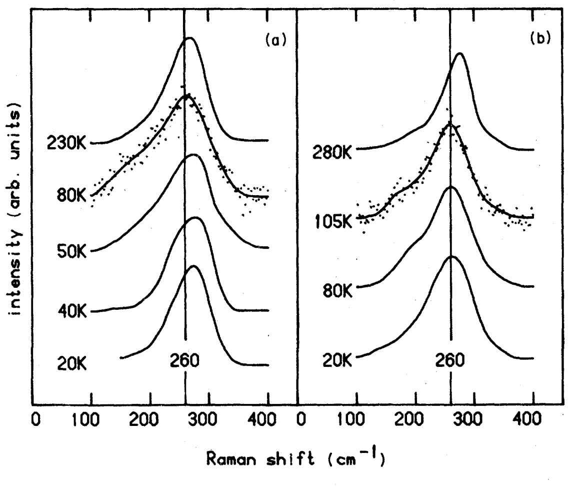

FIG. 1. E_g Raman scattering of transforming V_3Si (25 at.% Si) (a), and nontransforming V_3Si (24.1 at.% Si) (b), at different temperatures. For one curve of each set the measured points are given. The heights of the peaks are normalized for ease of comparison.

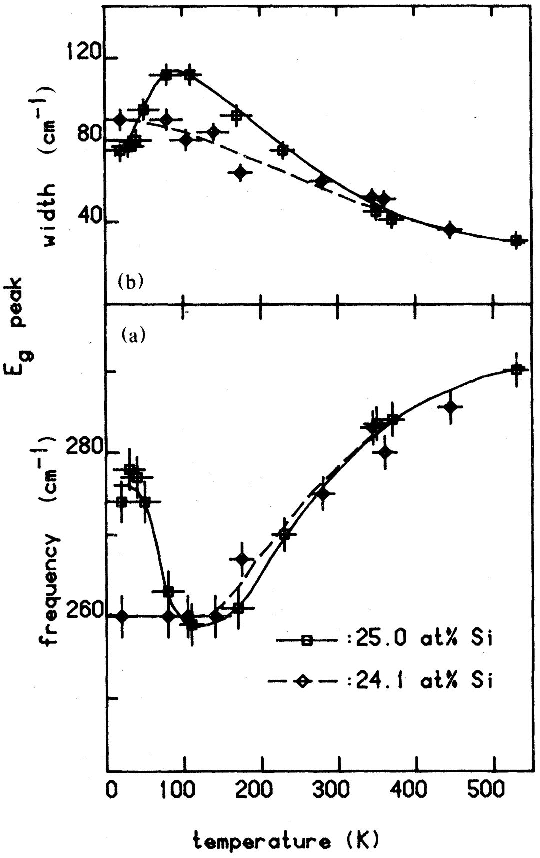

FIG. 2. Temperature dependence of frequency (a), and width (b), of the E_g Raman peak for transforming (25 at.% Si) and nontransforming (24.1 at.% Si) V_3Si.

changes its trend at ~90 K. From 400 to ~90 K the width increases strongly by a factor of about 3, whereas it decreases by ~35% when the temperature is lowered from ~90 to 20 K [Fig. 2(b)]. According to Fig. 2(b) for the nontransforming V_3Si sample the increase (factor ~2) of the width is much less pronounced than for the transforming sample. We find no decrease in width for nontransforming V_3Si at $T < 90$ K in contrast to the transforming crystal.

From a comparison of the bands in Figs. 1(a) and 1(b) it follows that, apart from defect-induced scattering, the Raman bands of the nontransforming V_3Si sample [Fig. 1(b)] are much more symmetric than the bands of the stoichiometric sample, which are particularly asymmetric in the temperature range from 40 to 110 K.

B. Nb_3Sn

1. Nb_3Sn spectrum

In Figs. 3(a), 3(b), and 3(c) for Nb_3Sn the Raman spectra of the three measuring geometries containing the symmetry species $A_{1g}+\frac{1}{3}E_g+F_{2g}$, E_g and F_{2g} are presented. The most intense line is the allowed E_g mode (192 cm^{-1}) shown in Fig. 3(b) in analogy to the situation found in V_3Si.[1,2] The F_{2g} spectrum has one prominent peak at 134 cm^{-1}. Whether this peak is an allowed mode [according to factor group analysis there are two Raman active modes $E_g(\Gamma_{12})$, $F_{2g}(\Gamma'_{25})$ in the $A15$ structure with space group O_h^3, $Pm3n$] or is due to defect induced scattering like in V_3Si can only be decided when several Nb_3Sn_x samples with different defect concentrations are available.[1] As to the $A_{1g}+\frac{1}{3}E_g+F_{2g}$ spectrum [Fig. 3(a)] there are no other prominent peaks than those already discussed together with the E_g [Fig. 3(b)] and F_{2g} [Fig. 3(c)] spectra. This result is consistent with factor group analysis giving no phonon mode of A_{1g} symmetry.

2. Temperature dependence of the Nb_3Sn E_g spectrum

The temperature dependence of the position and the width of the E_g peak are presented in Figs. 4(a) and 4(b). Similar to the situation in V_3Si [Fig. 2(a)]

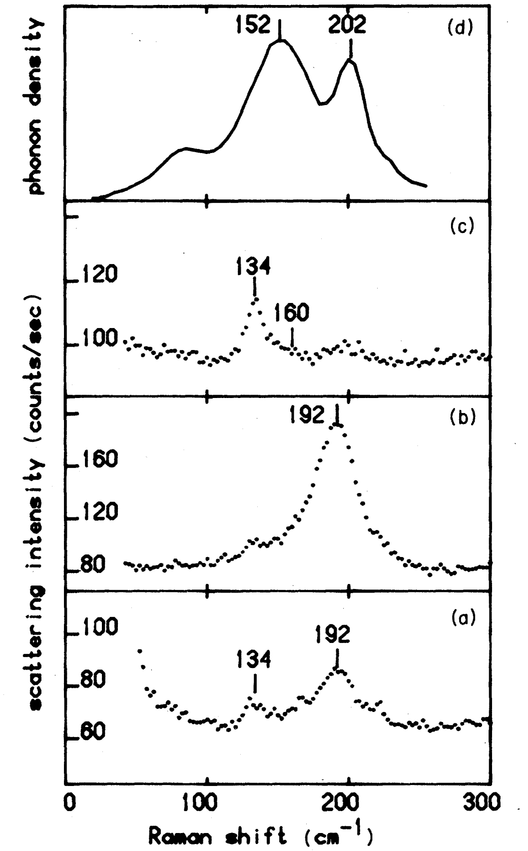

FIG. 3. Nb_3Sn: Raman spectra of three geometries giving $A_{1g}+\frac{1}{3}E_g+F_{2g}$ (a), E_g (b), and F_{2g} (c), respectively; phonon density of states (d) after Ref. 6.

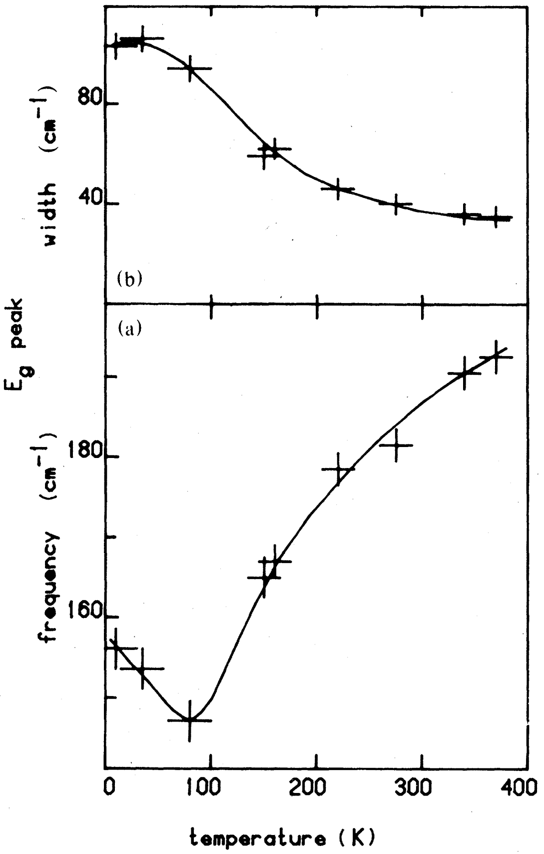

FIG. 4. Temperature dependence of frequency (a), and width (b), of the E_g Raman peak for Nb_3Sn.

with decreasing temperature the E_g mode first softens considerably and then the peak frequency increases at temperatures below ~ 80 K. The absolute and relative softening in Nb_3Sn is much stronger (from ~ 400 to ~ 100 K: 45 $cm^{-1} \triangleq 23\%$) than in V_3Si. In Nb_3Sn in comparison to the softening the increase in peak frequency is much weaker (~ 5%).

IV. DISCUSSION

Most interesting is the change in slope at ~ 100 K in the temperature dependence of the E_g peak frequency both in V_3Si ($\tilde{\nu}_{\min} \sim 260$ cm^{-1} at ~ 120 K) and Nb_3Sn ($\tilde{\nu}_{\min} \sim 150$ cm^{-1} at ~ 80 K) according to Figs. 2(a) and 4(a). The doubly degenerate optical mode of E_g symmetry which is Raman active ($q = 0$) involves transition metal atoms, lined up in chains in the *A*15 compounds, moving against each other in the same chain. This E_g mode is temperature dependent in the harmonic approximation.[3,4] A long-wavelength shear wave produces a movement of sublattices against each other. This shear mode is coupled to the sublattice motions corresponding to the E_g optical mode, thereby causing a tetragonal distortion. The E_g mode does not become unstable when the temperature is lowered because it would drive a shear acoustic mode unstable first.[3,4]

It has been known for some time that the elastic shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ and acoustical phonon modes in V_3Si and Nb_3Sn soften when the temperature is lowered.[7-9] From the work of Schweiss *et al.*[10] it follows that phonons with energies as high as ~ 160 and ~ 250 cm^{-1} for V_3Si and 160 cm^{-1} for Nb_3Sn soften when the samples are cooled from 300 to 77 or 5.6 K, respectively. This softening starting considerably above the martensitic transition (T_m for $V_3Si \sim 22$ K, $Nb_3Sn \sim 40$ K) is generally considered as a precursor effect to this transition. Thus a softening of the E_g mode[2] is consistent with this picture. What is surprising, however, is the increase in peak frequency at temperatures below ~ 100 K [Figs. 2(a) and 4(a)]. In addition, it seems strange that the minimum in frequency ($T_{\tilde{\nu}\min}$) is at a higher temperature (transforming V_3Si: ~ 120 K, Nb_3Sn: ~ 60–80 K) than the maximum in bandwidth ($T_{\mathrm{FWHM\,max}}$) (V_3Si: ~ 90 K, Nb_3Sn: ~ 40 K) (FWHM full width at half maximum). Furthermore one would expect the temperatures $T_{\tilde{\nu}\min}$ and $T_{\mathrm{FWHM\,max}}$, if they are in any way related to the martensitic transition, to be higher for Nb_3Sn than for V_3Si since $T_m(Nb_3Sn) > T_m(V_3Si)$.

Before the interpretation of our results, recent studies on transforming V_3Si by Hastings, Shirane, and Williamson[11] should be mentioned. These authors find from scattering of x rays having a penetration depth of as far as ~ 70 μm structural changes, i.e., a strong increase in width of Bragg peaks from ~ 60 to 25 K, falling off sharply below. No effect was seen from scattering of neutrons probing the entire sample. These observations are explained in terms of pretransition *d*-spacing fluctuations near the free surface. With our Raman measurements we are restricted to a penetration depth even smaller than in Ref. 11.

We interpret our results as follows: In addition to the Raman peak at higher temperatures [Fig. 1(a), temperature dependence see Fig. 2(a)] which is characteristic for the cubic structure there is a second Raman peak characteristic for the tetragonal structure at lower temperatures [Fig. 1(a), 20 K, 280 cm^{-1}]. This second peak contributes to the entire Raman structure when the temperature is lowered even at $T > T_m$. We believe that this second peak provides evidence for tetragonal structure above T_m. Tetragonal microdomains in bulk *A*15's have been suggested previously to exist above T_m.[12,13] Our model of tetragonal structure (microdomains) at $T > T_m$ is consistent with the data of Ref. 11, where it is explicitly stated that the picture of *d*-spacing fluctuations does not contradict the model of microdomains.

As to the question whether microdomains (*d*-spacing fluctuations) are present only down to depths of a few ten microns, as claimed in Ref. 11, Raman studies cannot provide a conclusive answer due to the limited penetration depth of the light of a few hundred Angstroms. From previous Raman investigations on transition metal compounds[6(a)-6(c)] and V_3Si (Ref. 1), where we found in general good coincidence of bulk properties such as superconducting transition temperature T_c and phonon density of states with Raman results, one may speculate that the microdomains also exist in the bulk of the sample.

Various support for our interpretation can be obtained. Testardi[14] has found several years ago that around 70 K *A*15 materials may not exhibit the cubic symmetry inferred from x-ray data for other methods such as acoustical measurements. More recently, Milewits and Williamson[15] found a broad temperature span within which the thermal expansion coefficient of V_3Si is anomalously large. They interpreted their results as evidence for tetragonality at temperatures extending up to at least 60 K. Harmonic sound generation by shear waves below 77 K found by Testardi[16] and large anharmonicities of V-atom motion in V_3Si at 78 and 13.7 K reported by Staudenmann and Testardi[17] may be connected with tetragonal domains.

We continue our interpretation in saying that the entire Raman band seems to have shifted to higher frequencies at low temperatures for transforming V_3Si because of the second peak mentioned above. Once most of the probed region consists of tetragonal structure (microdomains) the peak frequency does not increase any further. Indeed, the frequency of the Raman band at 20 K was found to be not higher than at 30 K. The scattering band is rather asymmetric [Fig. 1(a)] and the width of the entire structure of the Raman spectrum is large when at ~90 K both peaks (cubic: ~260, tetragonal: 280 cm^{-1}) make comparable contributions. At this temperature cubic and tetragonal regions are present in considerable quantities. At the higher temperature $T_{\tilde{\nu}\,\mathrm{min}}$ ($> T_{\mathrm{FWHM\,max}}$), where fewer tetragonal regions are present and the cubic structure still plays the predominant role, the contribution of the 280 cm^{-1} peak just compensates for the softening of the cubic structure leading to a minimum in the $\tilde{\nu}$-T curve [Fig. 2(a)]. When on the other side close to $T_m \sim 22$ K most of the lattice is tetragonal there remains only the high frequency peak at ~280 cm^{-1} and consequently the entire Raman structure is less asymmetric and the width is much smaller than at ~90 K. Consistent with this picture one can decompose the entire Raman structure into two components. A subtraction of the "tetragonal peak" at 20 K from the entire Raman peak, e.g., at 110 K indeed leads to a nearly Lorentzian structure at lower frequency believed to be the "cubic peak."

This interpretation takes care only of the strongly temperature-dependent contribution to the asymmetry, being particularly pronounced between 40 and 110 K in the stoichiometric sample [Fig. 1(a)]. There remains, of course, the broadness of the Raman band due to electron-phonon coupling and some further asymmetry, apart from defect induced scattering in the nonstoichiometric sample, over the entire temperature range. This behavior has been described in the work of Wipf *et al.*,[2] where the temperature dependent asymmetry was smaller than in our Fig. 1(a), as a Fano-type interference between phonon line and a continuum.

The situation in the nontransforming V_3Si (24.1 at.% Si) differs from the stoichiometric, transforming sample in the following way: the softening is not so pronounced as in the transforming sample. While a larger softening of transforming V_3Si compared to nontransforming V_3Si was observed in investigations of the elastic moduli below ~100 K (Ref. 7) we find this effect extended to ~250 K. Up to this temperature also the linewidths of the two samples differ [Fig. 2(b)]. The softening of the E_g mode comes to a standstill around 120 K. In the nontransforming sample there seems to be no or only a very weak tendency for forming tetragonal areas. Therefore, the higher frequency Raman peak (280 cm^{-1}) believed to be due to tetragonal domains does not show up. Possibly in the nonstoichiometric sample, defects or small distorted regions (increasing in number with decreasing temperature) stabilize the lattice,[12,13] thereby hindering the softening process. It should be noted that unlike in transforming V_3Si, where tetragonal areas lead to a quite asymmetric shape of the E_g peak, e.g., for $T = 80$ K, the peaks for the nontransforming V_3Si are nearly symmetric at all temperatures. This is further evidence for the lack of tetragonal structures (giving rise to a peak at ~280 cm^{-1}) in the nontransforming sample.

In our Nb_3Sn sample the softening down to 80 K is much stronger than in V_3Si both on a relative and an absolute scale. The reason for this strong softening in Nb_3Sn may be the stronger electron-phonon coupling in Nb_3Sn.[18] As to the change in slope in the $\tilde{\nu}$ vs T plot [Fig. 4(a)] the situation in our Nb_3Sn, which is not far from a stoichiometric sample, is between those observed in transforming and nontransforming V_3Si. There is a shift of the Raman structure to higher frequencies at temperatures around 40 K. Possibly there are tetragonal microdomains (second Raman peak ~160 cm^{-1}), although to a much lesser extent than in the transforming V_3Si sample. Since these tetragonal domains, probably of small size, are being formed with some difficulty, the change in slope in the $\tilde{\nu}$-T plot and the maximum in width occur at lower temperatures than in the transforming V_3Si sample. As to the fact that in our Nb_3Sn sample no tetragonal structure is detectable by x rays, we refer to our previous investigations on NbN where we found the sensitivity of the Raman probe superior to the x-ray method.[6(a)]

Summing up the discussion, we interpret our results as deriving from small tetragonal domains forming even at temperatures above 100 K. For detecting these domains Raman spectroscopy seems to be a very sensitive tool.

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