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Elastic behavior of transforming and nontransforming V_3Si

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The differences in the shear modulus and its isothermal pressure derivative for transforming and nontransforming crystals of V_3Si are explained in terms of a larger number of defects in the nontransforming samples. The defects give rise to microdomains of tetragonal distortions which stiffen the lattice for shear-type motion. The estimated defect concentration is consistent with the vacancy model proposed recently to explain the discrepancy between the sound-velocity and lattice-constant measurements for V_3Si as a function of pressure. The estimated ratio of vacancies in transforming and nontransforming variety agrees well with the ratio of the measured residual-resistivity ratios in these compounds.

A feature of the Martensitic structural transformation in the high-temperature superconductors V_3Si and Nb_3Sn is that the transformation does not take place in all samples of the material.[1,2] The shear modulus C_s and its pressure derivative show markedly different behavior for transforming and nontransforming samples. For nontransforming V_3Si, C_s shows less softening with decreasing temperature than the transforming variety,[3] and $(\partial C_s/\partial p)_T$ becomes large and negative near the transition temperature,[4] while for transforming samples the pressure derivative is positive and smaller.[5] The basic difference between the two types of samples has remained a puzzle, although a number of explanations have been suggested.[1,6]

In this paper we propose that the different type of behavior is due to the larger number of defects in nontransforming than in transforming crystals. The defects lead to the formation of microdomains of tetragonal distortions at a distribution of transformation temperatures. The distortions are of random orientations and are frozen in due to the energy barrier to go from one orientation to another. The nontransforming samples are thus pictured as "glassy" in the orientation of the tetragonal domains. On this basis, the word "nontransforming" has to be used with care. It is valid only in the sense that x-ray measurements do not see the microscopic tetragonal deformations. Presumably diffuse x-ray scattering can test our hypothesis.

This metastable picture of the nontransforming samples is suggested by the fact that they are generally part of the first-to-freeze portions of crystals grown from a melt,[1,2] and that it is possible (in Nb_3Sn) to convert nontransforming samples to the transforming variety by annealing.[7] The larger concentration of defects in the nontransforming samples is of course directly suggested by their poorer resistivity ratio, $\rho(300\text{ K})/\rho(20\text{ K})\simeq 10-20$, compared to $\simeq 40-80$ for the transforming samples.[1,2]

Defects serve as nucleating centers for the lattice deformation and as such would by themselves raise the transformation temperature for small concentrations.[8] It is only when the concentration is large enough and there is a wide enough distribution of local transformation temperatures ΔT_m, that the "glassy" state is realized and no macroscopic transformation is observed. It is hard to estimate the critical concentration of defects for this effect. We would guess that it arises when $k_B \Delta T_m$ becomes of the order of the surface energy of the domains.

We write the shear modulus for a nontransforming crystal C_s^{nt} as

$$C_s^{nt} = C_s^t + \eta C_s' + \eta^2 C_s'' + \dots , \tag{1}$$

where C_s^t is the shear modulus for a transforming crystal and η is related to the concentration of defects. For a nontransforming crystal, the effect of the microscopic tetragonal distortions is to stiffen the lattice, giving rise to a larger measured value of the shear modulus than for a transforming crystal. The macroscopic structural transformation temperature is lowered until it is preceded by the superconducting temperature, at which point the structural transformation is arrested.[2]

We calculate the isothermal pressure coefficients from Eq. (1) by retaining only the first two terms on the right-hand side, giving

$$\left(\frac{\partial C_s^{nt}}{\partial p}\right)_T = \left(\frac{\partial C_s^t}{\partial p}\right)_T + \left(\frac{\partial \eta}{\partial p}\right)_T C_s' + \left(\frac{\partial C_s'}{\partial p}\right)\eta . \tag{2}$$

The term $(\partial C'_s/\partial p)_T$ is bound to be of the same order of magnitude as $(\partial C^t_s/\partial p)_T$, so we ignore the last term in Eq. (2) and get from Eqs. (1) and (2),

$$\left(\frac{\partial \eta}{\partial p}\right)_T \eta^{-1} = \left[\left(\frac{\partial C^{\text{nt}}_s}{\partial p}\right)_T - \left(\frac{\partial C^t_s}{\partial p}\right)_T\right] \Big/ (C^{\text{nt}}_s - C^t_s)\,, \tag{3}$$

where all the quantities on the right-hand side have been measured as a function of temperature.[3-5] From Eq. (3) we get $(\partial\eta/\partial p)_T < 0$ for $\eta > 0$ for temperatures up to $T \simeq 100$ K, where $C^{\text{nt}}_s \simeq C^t_s$.

We describe the tetragonal distortion by an order parameter $\vec{\epsilon}$, and we have $\langle\vec{\epsilon}\rangle = 0$ for a nontransforming crystal, where we have taken the spatial average over the crystal and the orientation of the domains is assumed to be random. The average of the square of the order parameter does not vanish however, and for $\eta = \langle\epsilon^2\rangle$ we can evaluate the coefficient C'_s in Eq. (1) by writing the free energy in terms of one-electron energies which are strain dependent through the deformation potential, and using the constant density-of-states model.[9,10] The elastic constants are derived by expanding the free energy in powers of the strain. For the details of the calculation please see Ref. 10. For the observed difference $C^{\text{nt}}_s - C^t_s \simeq 1$ eV/atom at $T \simeq T_m$,[3] we get $\langle\epsilon^2\rangle \simeq 10^{-6}$, which shows that the root-mean-squared strain is of the order of the macroscopically observed tetragonal strain in transforming crystals. Experimental values for the anharmonicity also show that for uniform tetragonal distortions with $c/a - 1 = \pm 10^{-3}$ the change in the shear modulus is of the order of the difference between C^{nt}_s and C^t_s.[2] This lends empirical support to our estimate of $\langle\epsilon^2\rangle$.

We have assumed that the effect of the defects with the associated microscopic strains is to stiffen the elastic constants and thereby suppress the structural transformation, and that for V_3Si the number of defects is decreased with pressure. It is possible to obtain a similar effect on the elastic constants by assuming that the defects cause a smearing of the d-electron density of states. Hence a reduction in the number of defects with pressure would sharpen the variation in the density of states and cause the lattice to become more unstable. We believe that this effect is less important than the effect of the local strains, because there is little difference in T_c,[2] and $\partial T_c/\partial p$,[11,12] between transforming and nontransforming crystals.

A recent interpretation[13] of the experiment by Blaugher *et al.*[14] indicates that the defects in V_3Si are primarily vacancies, and that a vacancy concentration of about 1% (at room temperature) is "squeezed out" by a pressure of about 10 kbar. This interpretation is consistent with the large change in ductility observed in these crystals at similar pressures.[15]

In general we assume $\eta \propto (x^{\text{nt}} - x^t)$, where the nature of the defects is not specified. For vacancies we have $\partial(x^{\text{nt}} - x^t)/\partial p \simeq -1\%/10$ kbar at room temperature.[13] Using this value for $T \simeq T_m$ we get $(x^{\text{nt}} - x^t) \simeq 2\%$ from Eq. (3). The larger estimated vacancy concentration in nontransforming crystals is in agreement with the poorer measured resistance ratio, and provides support for the interpretation of the results of the anomalous lattice constant measurements[14] as due to vacancies in V_3Si.

In summary, the main result of this paper is that using a model in which defects seriously affect the elastic properties of the $A15$ class of compounds, the experimental results on the elastic constants and rate of variation of concentration of defects from Ref. 13 and Ref. 14, the ratio of vacancies in transforming and nontransforming V_3Si is quantitatively predicted. This ratio is found to be consistent with the residual resistivity ratios in these compounds. This lends considerable support to the ideas expressed in Ref. 13 and here.

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