Observation of Lattice Stabilization of V_3Si in High Magnetic Fields

J. P. Maita and E. Bucher
Bell Laboratories, Murray Hill, New Jersey 07974
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In V_3Si a noticeable reduction of the martensitic transformation temperature was found in high magnetic fields. The effect is in good agreement with recent predictions of Dieterich and Fulde, whose calculations are based on the linear chain model of Labbé and Friedel, thus giving strong confirmation of the latter also. Lifetime effects are also briefly discussed.

The effect of lattice instability due to strong electron-phonon couplings has first been discussed by Kohn and Vachaspati.[1] Later on, its influence on a variety of properties was evaluated more quantitatively[2-13] after the BCS theory[14] had been developed. It was shown that the lattice stability criterion is given by[2-4]

$$N(\epsilon_F)V_{BCS} < \tfrac{1}{2}. \quad (1)$$

It became clear that such lattice instabilities might be expected in high-temperature superconductors, or more precisely in materials with the largest T_c/Θ_D ratios. In particular, the group of $A15$ structure, V_3X and Nb_3X, displayed a certain number of additional unique features, such as large and strongly temperature-dependent susceptibilities and Knight shifts,[15,16] large electronic specific heats,[17] etc., suggesting extremely narrow d bands and high density of states,[16] thus favoring large electron-phonon coupling constants. The $A15$ structure also has the interesting property that it can be considered as a system of transition-metal ion chains in the (100), (010), (001) directions embedded in a bcc matrix.[18] Using this property and the tight-binding approximation, Labbé and Friedel[5] (referred to as L-F) proposed a band structure model for V_3Si, in which the $m = 0, \pm 1$ sub-bands are filled and with a Fermi level of $\approx k_B \times 21°K$[19] above the bottom of the $m = \pm 2$ sub-band. Near the bottom of the sub-bands the density of states is expected to diverge as $\sim(\epsilon - \epsilon_m^{(0)})^{-1/2}$, where $\epsilon_m^{(0)}$ stands for the bottom of the mth sub-band[5] (in the cubic phase). L-F demonstrated that in this class of materials a lattice instability will occur at low temperature if the Fermi energy is close enough to the bottom of the sub-band, leading to excessively high density of states with decreasing temperatures. The crystal then will distort spontaneously to a tetragonal unit cell at some temperature T_M, called the martensitic transformation temperature. The lowering of the symmetry leads to a splitting of the degenerate $m = \pm 2$ sub-band into two new sub-bands and, at the same time, to a lower density of states.

The nature of this instability has been considered by various authors[5,9-12,20] from different points of view in the recent past. We therefore felt it would be a challenging experiment to make a more rigorous quantitative test of the L-F model, in particular, in order to differentiate among other models. Recently, Dieterich and Fulde[21] investigated the influence of high magnetic fields on the martensitic phase transformation, basing their calculations on the L-F model. They found a shift of T_M to lower temperatures given by

$$\Delta T_M(H) = -0.18 T_M(0)[\mu_B H/\epsilon_F(0,0)]^2; \quad (2)$$

$\epsilon_F(0,0)$ stands for the Fermi energy at $T = 0$ and $H = 0$ in the cubic phase. $T_M(0)$ is the martensitic transformation temperature in zero field. After a brief description of the experiment we will discuss the results and compare them with the theoretical prediction and also with other models. For a variety of experimental reasons V_3Si was chosen: Its transformation temperature is in a convenient temperature range; its electronic parameters have been thoroughly analyzed; and the shift in T_M is expected to be among the largest in all $A15$ high-temperature superconductors.

It is most convenient to detect the martensitic transformation by specific heat,[22] which was measured by a heat-pulse technique.[17] The sample holder was fitted into an insert Dewar placed in a 2-in. bore of a Nb_3Sn superconducting solenoid, capable of generating 110 kOe. For reasons of field stability a fixed field of 90.0 kOe was chosen, measured by a Cu magnetoresistor. A silicon thermometer was calibrated in zero field against a Pt resistance thermometer, in turn calibrated at the National Bureau of Standards down to 10°K. In 90 kOe the silicon thermometer was carefully calibrated against the vapor pressure of liquid hydrogen. A cross check of the calibration curves

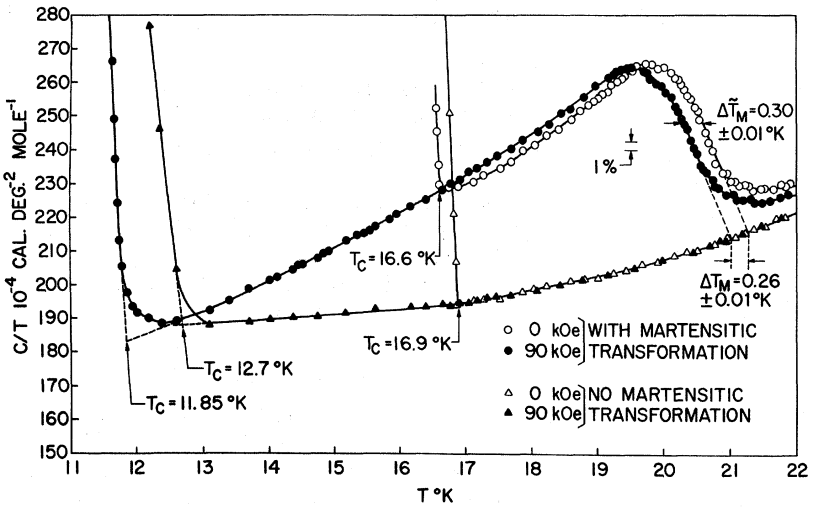

FIG. 1. Specific heat C/T of two V_3Si samples between 11 and 22°K in 0 and 90 kOe with and without martensitic transformation.

was made by measuring a test sample of high-purity copper (99.999%) in 0 and 90 kOe. The data agreed within better than 1% with Martin's values,[23] yielding no field dependence at all. Following this test two cylindrical samples ($\frac{5}{16}$ in. diam, $\frac{1}{4}$ in. long) of V_3Si were measured, both in 0 and 90 kOe. One was a very coarse-grained polycrystal, with a residual resistivity ratio (RRR) of 20 not showing any martensitic transformation, at least down to ~11°K. The other sample was a single crystal with a RRR of 60 showing a martensitic transformation in zero field at 21.3°K. The magnetic field was applied parallel to the cylinder axis, both coinciding with the 001 direction.

The results of the specific heat measurements are shown in Fig. 1. It provides an overall view of the specific heat in the temperature range of interest, including also the onset of the superconducting transitions in 0 and 90 kOe. In the specific heat, the transformation temperature T_M is not well defined. However, in our susceptibility measurements $\chi(T)$ shown in Fig. 2 we found a relatively sharp peak at (21.3 ± 0.1)°K. Therefore, we feel it is more convenient to define the transformation temperature T_M by the maximum in $\chi(T)$ of Fig. 2. It is interesting to note an almost rigid shift of the specific heat curve between the maximum and the onset of the increase in 0 and 90 kOe. Thus, specific heat fortunately measures a well-defined shift $\Delta\tilde{T}_M = -0.30$°K in 90 kOe, even though the transformation temperature T_M itself is less accurately defined. Due to the unsharp phase transition $\Delta\tilde{T}_M$ does not measure the true shift ΔT_M. ΔT_M is obtained as shown in Fig. 1.

For comparison we also show the specific heat and susceptibility of a nontransforming sample in Figs. 1 and 2. Above 30°K (not shown in Fig. 1) the specific heat values of the two samples are almost identical, whereas the susceptibility remains slightly lower in the nontransforming sample down to the superconducting transition temperature. The fact that neither a copper test sample nor the nontransforming V_3Si sample shows a detectable field dependence ($\lesssim 0.2\%$ rms) gives us considerable confidence regarding the accuracy of the field dependence of the transforming sample and also excludes any spurious effects. No irreversibilities could be detected in specific heat and susceptibility measurements which might be

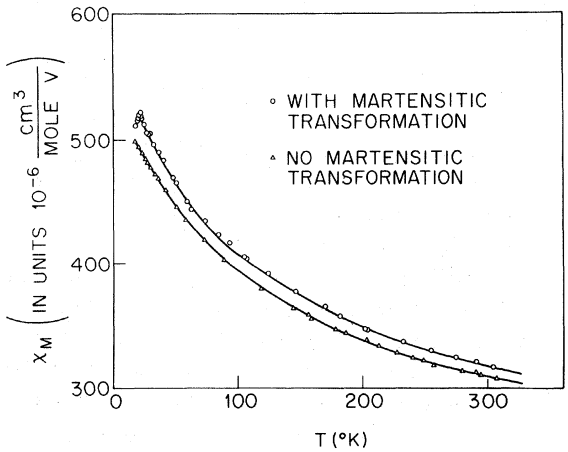

FIG. 2. Susceptibility between 17 and 300°K of the same samples as Fig. 1 [$H = 14.24$ kOe].

indicative of a first-order phase transition.

L-F have shown that the reason for the lattice instability is the excessively high density of states $N(\epsilon_F)$, increasing with decreasing temperature, which is a particular feature of certain $A15$-type compounds. At a critical density of states the crystal will spontaneously distort, lowering both its free energy and its density of states. This distortion is usually considered as a band-type Jahn-Teller effect.[5,9] The lowering of the density of states can be seen directly in Fig. 2. The temperature-dependent part of the susceptibility mainly reflects the (possibly exchange-enhanced) temperature dependence of the density of states due to the extremely low Fermi energy, e.g., $k \times 21°K$ in V_3Si, as analyzed from $\chi(T)$ and the linear chain model.[19] As Dieterich and Fulde[21] have pointed out, even moderate magnetic fields should have noticeable effects on the elastic properties of these materials via the field-dependent density of states, i.e., the Zeeman energies of the conduction bands. Using standard formalism and $N(\epsilon) \sim \epsilon^{-1/2}$, characteristic of the linear-chain model, they find at temperatures $T/\epsilon_F(0,0) \sim 1$ (where the martensitic transformation occurs) a decrease of the density of states with increasing field, due to the Zeeman splitting of the d conduction band [plotted as $\pi(T,H) = N(T,H)/N(0,0)$ in Fig. 1 of Ref. 21]. Therefore, in order to reach the critical density of states, i.e., the critical electron-phonon coupling driving the tetragonal distortion, one has to cool the sample correspondingly lower. This is exactly the basic physical origin of expression (2). With $T_M = 21.3°K$, $H = 90.0$ kOe, and $\epsilon_F(0,0)/k = 21°K$, (2) yields a value of $\Delta T_M = -0.31°$ K, in good agreement with our experimental value $\Delta T_M = -0.26°K$. We believe that this agreement very strongly supports the L-F model.

In order to amplify this point, we also discuss an alternative model proposed by Cohen, Cody, and Halloran.[8] From their square-well density-of-states model with a Fermi temperature $\epsilon_F(0,0)/k = 110°K$, in V_3Si, a shift of $-0.64 \times 10^{-2} T_M = -0.13°$ K is expected in 90 kOe.[24] This is a factor of 2 smaller than the experimental result and the prediction of the L-F model. The model of Cohen, Cody, and Halloran[8] nevertheless has been quite successful in fitting other experimental data such as susceptibility, electrical resistivity, elastic constants, and the strength of the phase transition.[8,25] However, our experiment clearly seems to be in favor of the physically much more realistic L-F model.

Next, we would like to discuss briefly the problem of transforming and nontransforming samples. Our results for ΔT_M are somewhat smaller than predicted by the L-F model. We have to keep in mind that for small Fermi levels of $\sim 10^{-3}$ eV, lifetime effects of the Bloch states become important and will smear out the singularity in $N(\epsilon)$, depressing the density of states at low temperature and even more so its field dependence. Replacing the L-F expression $N(\epsilon) = \frac{1}{2} B \epsilon^{-1/2}$ by $\frac{1}{2} B (|\epsilon| + U)^{-1/2}$ with a cutoff at $\epsilon = -U = (\hbar/l) V_F$, one finds for $kT/\epsilon_F(0,0)$ and $\mu_B H/\epsilon_F(0,0) \lesssim 1$

$$[\Delta N(T,H)/N(T,0)]_y = [\Delta N(T,H)/N(T,0)]_{y=0} \{1 + (2-\sqrt{2}) y^{1/2}\}^{-4}, \quad (3)$$

where $y = U/\epsilon_F(0,0)$ and $\Delta N = N_+ + N_- - 2N(H=0)$. Using $l \approx 5000$ Å and $m^* = m_e$ for our "clean" V_3Si single crystal we find $y \sim 0.02$ and $\{1 + (2-\sqrt{2}) y^{1/2}\}^4 = 1.37$. Therefore, mean free path effects can easily account for the difference between the experimental and theoretical value of ΔT_M. This also makes clear that the best samples will exhibit the highest values for both T_M and ΔT_M and that lifetime effects may reduce the density of states to below the critical value necessary for a martensitic phase transition.

One last interesting point needs consideration. If we assume for the moment no experimental upper bound on the magnetic field one may ask whether it is possible to stabilize the cubic phase down to $T = 0$. The answer is no. If we calculate $N(H)$ at $T = 0$ in the clean limit ($y = 0$) it is a simple matter to show that $\Delta N/2N(H=0) = \frac{1}{4} X^2/(1 - \frac{1}{4} \times X^2)$ with $X = \mu_B H/\epsilon_F(0,0)$, whereas at temperatures $T/\epsilon_F(0,0) \gtrsim \frac{1}{2}$, $\Delta N(H,T)/2N(0,T)$ is negative in a magnetic field. Thus the field dependence must reverse the sign at some temperature T_0 in the range $0 \leq T_0/\epsilon_F(0,0) \leq \frac{1}{2}$ and $T_M(H)$ will level off at T_0 in ultrahigh fields. On the other hand, this sign reversal suggests the possibility of inducing a martensitic phase transition at sufficiently low temperatures even in a nontransforming sample, provided $H \geq H_{c2}$. However, mean free path effects would affect this phenomenon in a destructive way as we have shown in (3). One would have to select a nontransforming sample as close as possible to the transformation conditions, i.e., with a high residual resistivity ratio. We hope that susceptibility measurements in very high fields will provide further clarification of such mean free path effects.

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Exciton Screening in Amorphous Mg-Bi and Mg-Sb Alloys*

John H. Slowik and Frederick C. Brown
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
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The Mg $L_{II,III}$ absorption edge ($h\nu = 50$ eV) has been studied as a function of composition in amorphous Mg-Bi and Mg-Sb alloys using a synchrotron source and a high-resolution grazing-incidence spectrometer. Exciton lines occur and are most prominent for low-conductivity material, e.g., corresponding to Mg_3Bi_2. Screening of the electron-hole interaction takes place as the conductivity increases, but a remnant enhancement remains at threshold even in pure Mg metal.

Certain intermetallic compounds exhibit striking composition-dependent electrical properties when in the liquid or amorphous state. For example, Ferrier and Herrell[1,2] have shown that the electrical conductivity of amorphous Mg_xBi_{1-x} and of Mg_xSb_{1-x} is quite low and cusplike at $x = 0.60$ (e.g., amorphous Mg_3Bi_2) and rises to metallic values on either side of this composition. We find that sharp exciton lines occur at the Mg $L_{II,III}$ absorption edge in the extreme ultraviolet (50 eV) for low-conductivity amorphous films. These exciton lines tend to be screened out with increasing conductivity, but a remnant enhancement remains at threshold even in pure Mg metal.

The spectra were obtained by measuring the transmission of synchrotron radiation through thin films using a high-resolution grazing-incidence monochromator.[3] The amorphous films (90–510 Å thickness) were made *in situ* by coevaporation onto Formvar substrates kept near 100°K by baffles at liquid-nitrogen temperature. Composition x could be controlled to about 1 or 2% by means of crystal thickness monitors and circuitry developed to display accurately the ratio of evaporant fluxes. Thermal flux was minimized by means of baffles and large source-to-substrate distances (1 m). The amorphous Mg-Bi alloys could be transformed to crystalline simply by slowly warming to room temperature.

Figure 1 shows the absorption spectra for several amorphous Mg_xBi_{1-x} films of different composition x. The instrument spectral bandwidth was less than 0.02 eV. These spectra are all