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Structural transformation of near-equiatomic V-Ru compounds at high pressure

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The structural transformation of near-equiatomic V-Ru compounds has been studied resistively under hydrostatic pressure up to ~21 kbar. It is found to be suppressed by the application of pressure. The rate of suppression increases as the Ru content approaches the critical concentration for the occurrence of the transformation. A critical pressure of 14 ± 2 kbar is obtained for the stabilization of the cubic phase down to 0 K in a sample containing 46-at.% Ru. The results are interpreted as support for the suggestion that the enhanced superconductivity in this compound system is associated predominantly with the singular feature of its electron energy spectrum.

I. INTRODUCTION

The crystal lattice of near-equiatomic V-Ru compounds with Ru concentration C larger than a critical value $C_k \simeq 45.5$ at.% undergoes a cubic $B2$ (CsCl) to tetragonal $B2$ transformation upon cooling.[1] The structural transformation temperature T_L increases rapidly with increase of C. C_k is also associated with the dramatic appearance of superconductivity, with the superconducting transition temperature T_c peaking sharply about it.[1–3] The structural transformation is accompanied by an anomalous behavior of the electrical resistivity,[1] magnetic susceptibility,[1] and Knight shift[4] of ^{51}V. From the form of these anomalies, it was proposed[1,4] that the structural transformation is electronic in nature and results in a large drop in d-electron density of states in going from the cubic to the tetragonal phase. Alternatively, on the basis of his sound-velocity measurements, Testardi[5] has suggested that the T_c peak at C_k is caused by the softness of the lattice.

The concurrence of structural transformation and high-temperature superconductivity has stimulated extensive investigations both experimental and theoretical on these two phenomena, particularly for the $A15$ compounds, where attempts have been made to account for the high T_c of these compounds.[6,7] Some approaches have emphasized the fine structure of the d-electron subbands, characteristic of the peculiar linear-chain arrangement of the transition-metal atoms in these compounds. Others have treated the softness of lattice, which ultimately leads to the structural transformation, as the dominant factor. While the former, which is specific to the $A15$ compounds, is capable of accounting for the signs of the pressure dependences for T_c for V_3Si $(\partial T_c/\partial P > 0)$[8,9] and Nb_3Sn $(\partial T_c/\partial P < 0)$,[8,10,11] provided the appropriate assumptions are made regarding the d-subband occupation and its variation with pressure,[11] the latter[12] predicts a general quadratic pressure dependence for T_c, with a maximum T_c at a pressure where $T_c = T_L$. While any deviation from linearity of the measured variation[8,9] of T_c with pressure for V_3Si is at least an order of magnitude less than that predicted,[13] the measurements do not extend to high enough pressure to test the possibility of T_c passing through a maximum at T_L.

Measurements[14] of the variation of T_c and T_L under pressure for a range of $Hf_{1-x}Zr_xV_2$ compounds are also consistent with $\partial T_c/\partial P > 0$ for $\partial|T_L - T_c|/\partial P < 0$, but again the pressure does not reach that required for $T_c = T_L$.

In order to examine further the interrelationship between T_L and T_c we have undertaken a high-pressure study of the near-equiatomic composition alloys in the V-Ru system. Although these compounds can hardly be regarded as high-T_c superconductors, their maximum $T_c \sim 5.5$ K is high relative to their structure class. Other than the V-Ru system, only a very limited number of superconductors with $B2$ structure has been found and none of these has a T_c greater than 3 K.[15]

A detailed account of the influence of pressure upon T_c for the V-Ru compounds has already been presented.[3] The present paper extends a preliminary report[16] on the pressure dependence of T_L, as determined from measurements of the electrical resistivity as a function of temperature at fixed pressure up to ~21 kbar for samples with $C = 46$, 47, and 48. These results are related to the previous conclusions, which were based upon the T_c measurements[1,3,4] regarding the nature of the influence of the structural distortion upon T_c.

II. EXPERIMENTAL

Three samples ($C=46$, 47, and 48) of length ~3 mm and cross section ~0.6 mm^2 were cut from the V-Ru buttons prepared for the experiments in Ref. 1. Pt leads were spot-welded onto the samples. A standard four-lead technique using a PAR HR-8 lock-in amplifier was employed to measure the electrical resistivity ρ at 28 Hz. No difference between this low-frequency ρ and the dc ρ was found. The temperature was determined by a Au + 0.07-at.%-iron-Chromel thermocouple for the sample with $C=46$, and by a Chromel-Alumel thermocouple for the samples with $C=47$ and 48. The Chromel-Alumel thermocouple was calibrated against the Au + 0.07-at.%-iron-Chromel thermocouple[17] at low temperature and atomspheric pressure. To determine the T_c, a Ge resistance thermometer was used. The hydrostatic pressure environment was provided by a fluid mixture of 1 : 1 *n*-pentane and isoamyl alcohol (for $C=46$ up to 21 kbar) or 1 : 1 kerosene and silicone oil (for $C=47$ and 48 up to 12 kbar). The clamp technique was employed to contain the pressure which was generated in a press at room temperature. The high-pressure clamp was then removed from the press and cooled slowly inside the cryostat. A superconducting Pb-manometer[18] situated next to the sample was used to determine the pressure at low temperature for $C=46$. For $C=47$ and 48, the pressure was determined at room temperature by a gauge which had been calibrated against the 25.4-kbar Bi transition. No correction to these values was made to allow for the small pressure loss[19] which occurs on cooling due to the freezing of the medium. The electrical leads were brought out from the high-pressure cell through a Stycast 2850 FT Epoxy seal.[20]

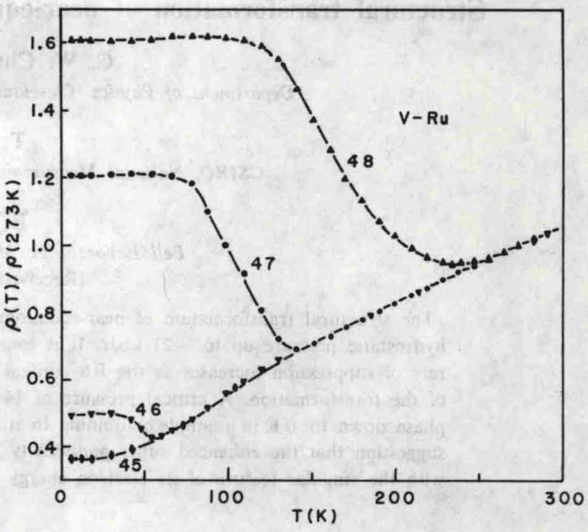

FIG. 1. Temperature dependence of the normalized resistivity. The numbers represent the atomic percent of Ru.

III. RESULTS AND DISCUSSION

We have measured and show in Fig. 1 the temperature dependence of ρ at atmospheric pressure normalized to its value at 273 K for samples with $C=45$, 46, 47, and 48. The normalized resistivity ρ_n initially follows the normal metallic behavior and decreases upon cooling, but then rises rapidly at a temperature which depends strongly on C and finally levels off. It has been demonstrated[1] that this anomalous rise is ρ_n is associated with the cubic to tetragonal strucutral transformation. Since the general temperature dependence of ρ_n prior to the transformation is similar for all samples, the form of ρ_n for the sample with $C=45$, which behaves normally, is considered to be representative of that expected for samples with $C>45$, had there been no structural change. Hence one may estimate the fractional change in ρ_n due to the transformation for different values of C. It is evident from Fig. 1 that the fractional change of ρ_n increases with C in accord with the changes observed for the other electronic properties.

The three samples with $C=46$, 47, and 48 were studied under hydrostatic pressure. At temperatures above the structural transformation ρ was found to be independent of compression to within ±3% up to ~21 kbar. Typical results are represented by those for the sample with $C=46$ shown in Fig. 2. Here we have plotted ρ, normalized to that at 72 K, as a function of temperature at the pressure, in kbar, denoted by the number associated with each curve. All curves vary in a similar way before the anomalous rise in ρ begins to appear. For $P \geq 15$ kbar, no ρ anomaly was detected above T_c. Between ~15 and ~21 kbar, ρ_n at 10 K decreases slightly with pressure, but by no more than 4%, and all ρ_n-vs-T curves fall into the shaded region in Fig. 2.

In Ref. 1 the lattice distortion for the V-Ru compounds was characterized by a transformation temperature T_L, defined to be the temperature at which the minimum in ρ occurred. While it is clear from Fig. 2 that T_L, defined in this manner, is displaced towards lower temperature under pressure, it is difficult to determine the exact P dependence since the anomaly in ρ is suppressed under pressure, particularly for the sample with $C=46$. To better describe the P effect on the structural transformation, we have considered a quantity $\Delta\rho_n$ as a measure of the fractional change in electronic properties due to the transformation. Because of the similar behavior of ρ_n prior to the appearance of the transformation both with and without pressure,

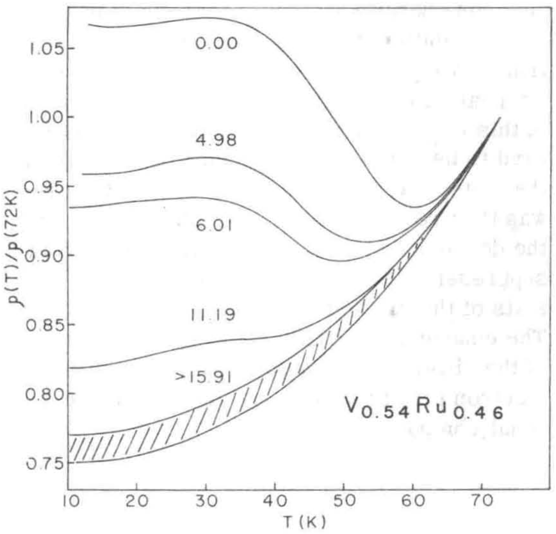

FIG. 2. Effect of pressure on the normalized resistivity of $V_{0.54}Ru_{0.46}$. The numbers denote the pressure in kbar.

$\Delta\rho_n(P, C)$ may be most conveniently taken as $\rho_n(P,C) - \rho_n(15, C)$ for $C = 46$, and $\rho_n(P, C) - \rho_n(0, 45)$ for $C = 47$ and 48. To be consistent, all $\Delta\rho_n$'s have been evaluated at 10 K, where ρ_n varies with temperature slowly. The results are shown in Fig. 3 where $\Delta\rho_n(P)/\Delta\rho_n(0)$ is plotted against P. For $C = 46$ a critical pressure, $P_k = (14 \pm 2)$ kbar, is obtained for the complete suppression of $\Delta\rho_n$, which we associate with the stabilization of the cubic phase. From an examination of Fig. 2 it can be seen that the indications are that T_L follows a strongly nonlinear variation with pressure, particularly close to P_k. However, we are unable to distinguish whether T_L actually falls to zero at P_k or whether the transformation is suppressed before this occurs. For $C = 47$ and 48, the extrapolated P_k is much higher than 21 kbar, the maximum hydrostatic pressure available in the present investigation. It is evident from Fig. 3 that P_k increases rapidly with C.

The T_c of the sample with $C = 46$ was determined resistively up to 21 kbar, and the variation is shown in Fig. 4. The vertical bar attached to each point represents the transition width and the number indicates the sequential order in which the data were taken. When detected inductively the superconducting transition is wider than that seen resistively and shows a small step below 4 K, suggesting the inclusion of small amount of a second phase (see Ref. 3 for a comprehensive description of the inductive transition curves). However, the bulk of the inductive transition agrees with the resistive one. T_c initially increases linearly with pressure with $\partial T_c/\partial P = (9.1 \pm 0.3) \times 10^{-6}$ Kbar^{-1}, but an abrupt change of slope occurs at (14 ± 2) kbar, coincident with P_k, the critical pressure above which the structural transformation is prohibited. This observation confirms the earlier assumption[3] that such changes in the rate of change of T_c with pressure are associated with the suppression of the cubic to tetragonal transformation.

Our present value for the initial $\partial T_c/\partial P$ for $C = 46$ is smaller, by about a factor of 2, than that obtained from the previous independent measurements[3] made on a different sample of this nominal composition. However, in view of the large variation of $\partial T_c/\partial P$ with C which occurs near $C_k = 45.5$, we would attribute the difference to a possible small difference in C.

Based on the general occurrence of elastic anomalies in high-T_c superconductors, Testardi[12] has suggested that a high T_c is associated with a lattice softness. According to this suggestion the highest T_c should occur when the lattice softness is at a maximum. Thus, if $|T - T_L|^{-1}$ is adopted as a measure of the lattice softness at temperature T, then it would be anticipated that T_c would reach a maximum as $T_c \to T_L$. The observation of the T_c peak at

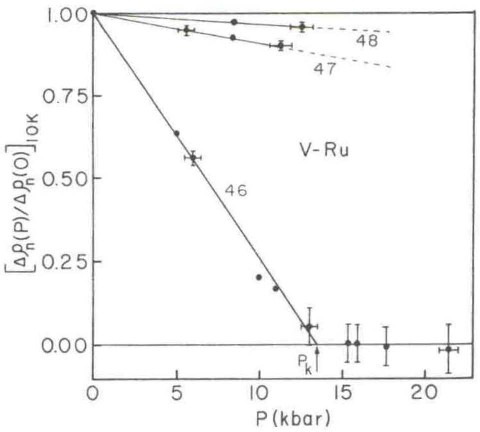

FIG. 3. Pressure dependence of $\Delta\rho_n$. The numbers represent the atomic percent of Ru.

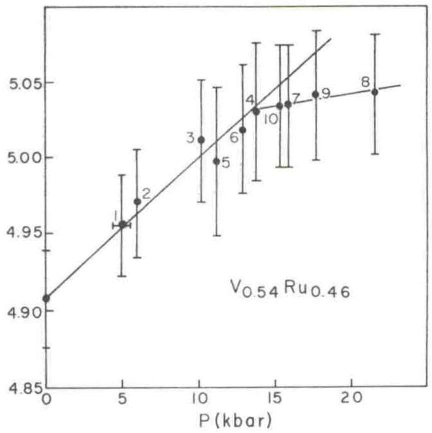

FIG. 4. Pressure dependence of T_c for $V_{0.54}Ru_{0.46}$.

C_k seemed to be consistent with this explanation.[5] However, the expected T_c maximum at a pressure close to P_k fails to appear, but instead a continuous increase of T_c with pressure beyond P_k is found, although at a slower rate.

It has been observed[1] that over a narrow temperature region where structural transformation takes place, the electrical resistivity increases sharply and the magnetic susceptibility decreases rapidly upon cooling. In addition, the Sommerfeld coefficient γ of the specific heat peaks,[1,2] at C_k. From these results it was suggested[3,4] that the structural transformation is driven by the excess electron energy associated with a large value of the d-electron density of states $N(0)$ at the Fermi surface for the electron energy spectrum of the cubic phase. The transformation then results in a substantial reduction in $N(0)$, which accounts for the appearance of a γ peak near C_k. The enhanced superconductivity in this compound system near C_k was thus considered to be a direct consequence of the existence of the $N(0)$ peak. The increase of T_c under pressure was then readily accounted for by the increase in the density of states which would result from the suppression of the tetragonal distortion. The results of the present study support this suggestion. The change of $\partial T_c/\partial P$ for $P \geq P_k$ is then a reflection of the difference in the pressure responses of the electron energy spectra between the cubic and tetragonal compounds.

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