

Superconductivity and structural instability of the ZrV₂ compound

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The electrical resistivity between 60 and 300 K and the superconducting transition temperature T_c are measured for samples of Laves-phase ZrV₂ with a C15 structure in quenched and annealed states. It is found that a structural transformation occurs at ~ 90 K in the annealed samples, whereas their T_c is 0.3° lower than for the quenched samples. The appearance of lattice instability and the lowering of T_c as a result of annealing at 1200°C is ascribed to an increase in the degree of atomic ordering in the crystal lattice of the ZrV₂ compound.

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Much attention is being paid lately to the problem of the interrelationship between superconductivity and lattice instability in compounds of the transition metals.^[1,2] The interest in this problem is explained by the fact that high superconducting transition temperatures T_c occur, judging by numerous experimental data,^[3-6] in intermetallic compounds with an unstable crystal lattice, although, apparently, there exists no mechanism at all for "an enhancement of superconductivity by structural instability."^[2]

One must assume that considerable light could be shed on the question of the presence of a correlation between lattice instability and superconductivity by measurements of T_c in superconducting intermetallic compounds of identical chemical composition and crystal structure, but differ by whether or not a phase transition connected with a structural instability is realized in them.

In the present work we have successfully identified a class of objects in which the presence or absence of a structural transformation preceding the superconducting transition is determined solely by the character of the heat treatment of the samples. We have in mind the superconducting Laves phases of type MgCu₂ with a C15 structure (space group $O_h^1-Fd\bar{3}m$), in which first-order phase transitions are observed at $T_m \gg T_c$, accompanied by a lowering of the symmetry of the crystal lattice.^[7-9] In the present work the investigated samples were Laves-phase ZrV₂.

The intermetallic-compound samples were prepared by a method for alloying zirconium and vanadium in an arc furnace with a permanent electrode in an atmosphere of purified argon. The resulting ingots were cut with an electric-spark lathe. Some of the samples were

annealed in a vacuum of $\sim 10^{-6}$ Torr at 1200°C over a period of 24 hours. In the x-ray patterns of both the annealed and the unannealed samples contained only lines of the cubic phase of type C15 with parameter $a = 7.438 \pm 0.002$ Å.

The results of measurements, at 60–300 K, of the relative resistivity of the samples after arc melting (I) and of samples which had undergone additional annealing at 1200°C (II) are presented in Fig. 1. It is clear that the $\rho(T)$ curves for the samples ZrV₂(I) and ZrV₂(II) are quite different¹⁾: The temperature dependence of the resistivity of the annealed sample has a distinct maximum at ~ 90 K (with rising temperature); on the curve for the unannealed sample there are no anomalies what-

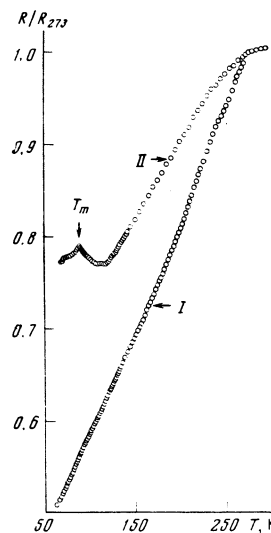


FIG. 1. Temperature dependence of the resistivity of ZrV₂: I—sample after arc heating, II—sample annealed in a vacuum at 1200°C for 24 hours.

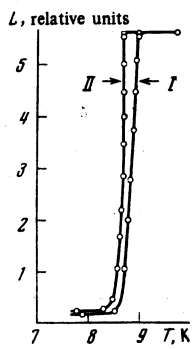


FIG. 2. Curves of the superconducting transition of samples of ZrV_2 . The ordinates represent the inductance of the measuring coil.

soever. It is significant that the position and shape of the maximum in the plot of $\rho(T)$ for ZrV_2 (II) depends on the direction of change of the temperature: in measurements "while cooling" the maximum shifts by 10–15° to the low-temperature side; in this case the anomaly in the plot of $\rho(T)$ is more strongly pronounced. Both the character of the temperature dependence of the electrical resistivity and the presence of hysteresis effects clearly indicate that a phase transition of the first order takes place in the ZrV_2 (II) samples, which were annealed at 1200 °C, owing to loss of stability of the crystal lattice. In the plots of $\rho(T)$ for the unannealed ZrV_2 (I) samples there is no indication whatsoever of a phase transition.

In Fig. 2 are shown curves of the superconducting transition for both samples of ZrV_2 , obtained by an inductance method. A relatively small, but clearly pronounced rise in T_c is evident in the case of the unannealed sample: $\Delta T_c \sim 0.3^\circ$. The width of the transition is very small and essentially does not depend on the prior heat treatment.

Obviously, both the connection of the appearance of the loss-of-stability effect of the ZrV_2 crystal lattice with the heat-treatment conditions, and the influence of the heat-treatment conditions on the superconducting transition temperature, can be ascribed to one and the same cause: the difference in the degree of atomic ordering of the crystal lattices of the annealed and unannealed samples. Actually, in a crystal lattice of type C15 the Zr and V atoms occupy the crystallographically inequivalent sites 8(a) and 16(d). One may propose the possibility of an occasional exchange of atoms occupying different lattice sites, analogous to the effect which takes place in superconductors with an A15 structure.^[10,12]

If we represent the compound ZrV_2 in terms of the structural formula $(V_x Zr_{1-x}) [V_{2-x} Zr_x]$, in which the atoms at a-sites are in the parentheses and those at d-sites in the square brackets, then the Bragg-Williams-Gorskii parameter^[11,12]

$$S = \frac{p-r}{1-r}, \quad (1)$$

[where p is the probability of finding an atom of a given kind at specific crystallographic sites ($p_{Zr} = 1-x$, p_V

TABLE I.

$h^2+k^2+l^2$	F_0	F_1
$32n$	$f_{Zr} + 2f_V$	0
$16n+11$	$2^{1/2} f_{Zr}/2 + f_V$	$(-2^{1/2}-1)(f_{Zr}-f_V)/2$
$16(2n+1)$	$f_{Zr}-f_V$	$-2(f_{Zr}-f_V)$
$32n+12$	$2f_V$	$f_{Zr}-f_V$
$16n+8$	f_{Zr}	$-(f_{Zr}-f_V)$
$16n+3$	$2^{1/2} f_{Zr}/2 - f_V$	$(2^{1/2}+1)(f_{Zr}-f_V)/2$

$= 1-x/2$), r is the proportion of atoms of a given kind in the alloy ($r_{Zr} = \frac{1}{3}$, $r_V = \frac{2}{3}$) is linked to the quantity x by the relationship

$$S = 1 - 3/x. \quad (2)$$

It is also easy to demonstrate that a change in the parameter S significantly affects the x-ray interference intensity. The intensity I is proportional to the square of the structural amplitude F , which equals

$$F = \sum_{n=1}^N f_n \exp 2\pi i (hx_n + ky_n + lz_n), \quad (3)$$

where f_n is the atomic scattering factor of the n -th atom, and the sum is over all atoms in the unit cell ($n=24$ for ZrV_2). For $(V_x Zr_{1-x}) [V_{2-x} Zr_x]$ the dependence of the structural amplitude on the ordering parameter S can be represented in the form

$$F = F_0 + F_1 x. \quad (4)$$

Here F_0 is the value of the structural amplitude in the case of complete ordering ($x=0$, i.e. $S=1$). The second term in Eq. (4) depends directly on x . At the same time the character of the dependence of F_1 on x is different for different combinations of the indices (hkl) of the reflection planes (see Table I).

It was already pointed out above that only diffraction lines of a type-C15 phase were present in the x-ray patterns of both the annealed and the original samples. However, the intensities of the various x-ray interference lines differed significantly (Fig. 3 shows segments of the x-ray patterns of the samples, obtained on a DRON-1.5 instrument with CuK_α radiation). An increase in the intensity ratios $I_{(111)}/I_{(311)}$ and $I_{(220)}/I_{(311)}$ and a decrease of $I_{(222)}/I_{(311)}$ is clearly evident in the case of the ZrV_2 (II) sample annealed at 1200 °C. In accordance with the data in the table, this implies a pronounced decrease in x , i.e. an increase in the Bragg-Williams-Gorskii parameter of the ZrV_2 sample that underwent the high-temperature vacuum heat treatment.

One must assume that a change in the ordering parameter S leads also to a change in the electronic density of states. In the case of the structure of greater order, ZrV_2 (II), a condition necessary for the appearance of structural instability is evidently realized, namely proximity of the singularity of the density of states in the vicinity of the point $X(0, 0, 2\pi/a)$ of the Brillouin zone to the value of the chemical potential. For severe structural disorder, as in ZrV_2 (I), this condition need

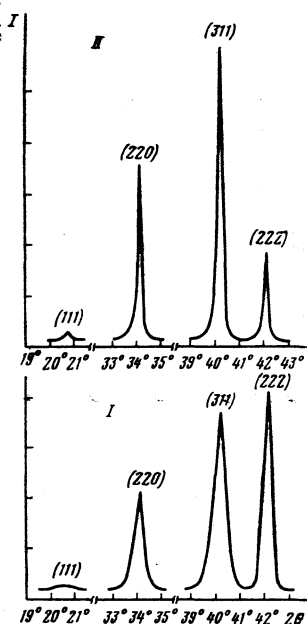


FIG. 3. Diffraction patterns of the ZrV_2 samples. Diffractometer DRON-1.5, CuK_α radiation, scanning through a diffraction angle 2θ in steps of 0.1° .

not necessarily be fulfilled. In this connection, the discrepancy in the published data on to the presence of a structural instability in superconducting compounds with structure C15 and the strong differences between the values of T_m for these compounds may be due to the different degrees of atomic ordering in the samples.

The results of the comparative investigation of samples of the superconducting Laves-phase ZrV_2 with different degrees of atomic ordering indicate a decrease of T_c with increase of S , brought about by the onset of a structural-instability mechanism. This, it would seem, contradicts the observed regularity in superconducting compounds with A15 structure, whereby an increase in S leads to a sharp increase in the superconducting transition temperature.^[13] It is apparently necessary, for all superconducting compounds, to consider the presence of two competing processes due to a change in the degree of atomic ordering: a decrease in T_c as

a result of a loss of stability of a high-symmetry crystal lattice and an increase in T_c due to an increase in the efficiency of formation of chains of transition-metal atoms. However, it is not ruled out that for superconductors with C15 structure, in whose crystal lattices the transition metal atoms form a branched space lattice, the latter process does not play as significant a role as for high-temperature superconductors with an A15 structure.

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- ¹We note that the resistivities of samples I and II at room temperature are essentially the same ($\sim 5.4 \times 10^{-3} \Omega \cdot \text{cm}$).
²Even closer to the effect under consideration is the well-known phenomenon of "inversion of spinels," wherein different atoms exchange places, since the configuration of the metallic atoms in spinel lattices AB_2X_4 and in Laves phases of the type $MgCu_2$ is identical.

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