both frequencies $f_p^{(3)}, f_p^{(4)}$ leads to a substantial modulation of the amplitude of the pulsed sequences with the difference frequency $f_p^{(4)} - f_p^{(3)} = 89$ kHz (Fig. 6f).

We note in conclusion that the foregoing analysis can be generalized to include three-dimensional lattices. In particular, in the case of a logarithmic nonlinearity it is possible to obtain the exact solution of three-dimensional equations similar to (1). These solutions correspond to a soliton whose front is oriented at various angles to all three axes of the lattice. Such a soliton is shorter by a factor $\sqrt{3}$ than the soliton propagating along one of the axes.

The singularities of the propagation and resonant excitation of solitons in anisotropic nonlinear lattices, which were considered above, can apparently play a substantial role in the analysis of various types of collective excitations in a solid. As already indicated, the importance of the soliton concept in the explanation of energy transport processes and transport of thermal excitations in crystals was recently made clear.[11,12] In recent papers by Bishop (see Ref. 13 and the bibliography therein) used the methods of statistical mechanics to analyze the contribution of the soliton component to the lattice oscillations. On the basis of the results of the present paper one can expect the anisotropy of the soliton parameters to influence the thermodynamic properties of nonlinear lattices. At the same time, crystals of a definite regular shape (for example, cubic) can be singled out under corresponding boundary conditions in that respect, that it is possible to excite effectively in them soliton modes of high intensity.

[1)]For a travelling plane wave this leads, as usual, to the Kortweg-de Vries equation.

[2)]A more general approach should include in the analysis, in place of solitons, periodic (conoidal) waves, this would make it possible to describe oscillations of any amplitude.


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# Phase transitions in superconducting compounds with superstructure *C*-15


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The crystal structure of the superconducting compounds $ZrV_2$ and $HfV_2$ with *C*-15 structure is investigated at 77–300 K, and the temperature dependence of their electric resistance is investigated at 61–300 K. At $T_m = 80$ K (for $ZrV_2$) and $T_m = 100$ K ($HfV_2$) the cubic lattice symmetry is lowered to a rhombohedral and tetragonal, respectively, an abrupt change takes place in the atomic volume, and maxima appear on the temperature dependence of the resistivity. Inflections of the temperature-dependence curves of the crystal lattice parameter and of the resistance are observed at $\sim 157$ K ($ZrV_2$) and $\sim 120$ K ($HfV_2$). It is suggested that the loss of stability of the crystal lattice is the result of two successive phase transitions, one of the second order and the other of first order.



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Much attention has been paid of late to the study of lattice instability of superconducting Laves phases with *C*-15 structure (in particular $ZrV_2, HfV_2$). Interest in the question is quite understandable: $ZrV_2, HfV_2$, the ternary compounds $Zr_xHf_{1-x}V_2, Hf_xTa_{1-x}V_2$, and others are unique examples of a very strong difference between the critical temperatures of the transition to the superconducting state ($T_c \sim 10$ K) and the temperatures at which the cubic crystal lattice of the type *C*-15 lose stability ($T_m \sim 100$ K). The existence of such a situation uncovers extensive prospects for experimental and theoretical study of the relation between the two phenom-



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ena of structural instability and superconductivity.

The changes of the crystal structure[1-4] and of the thermal[5,6], elastic[4,7-9], electronic,[4,6,10-14] and of other properties of these compounds near $T_m$ have by now been well investigated. Two circumstances call attention to themselves: the very large (up to 80 K!) scatter of the values of $T_m$ obtained from measurements of different physical properties, and the contradictory nature of the opinions on the thermodynamic singularities of the transformation at this point (thus, the heat capacity gives a λ anomaly characteristic of second-order phase transitions, while the atomic volume changes jumplike, a property of first-order transitions, ect.) Whereas the first circumstance can still be related to differences in the structural state of the investigated samples, the presence of a true or apparent difference in the "order" of transition in $T_m$ undoubtedly calls for a detailed analysis.

In our opinion, much information can be obtained from parallel structural investigations of compounds with $C$-15 structure and from measurements, made on one end the same sample, of properties that are sensitive to changes of the electronic energy spectrum, in the temperature range that includes $T_m$. The main content of the present article is in fact an analysis of the results of x-ray study of the crystal structure of the compounds $ZrV_2$ and $HfV_2$ at 77–300 K and of the measurement of their electric resistance at 61–300 K.

The manner of obtaining single-phase polycrystalline samples and the research procedure were described earlier.[3,13] Annealing of $ZrV_2$ at 1200 °C for 272 hours and of $HfV_4$ at 1200 °C for 24 hours resulted in a high degree of atomic ordering (the Bragg-Williams-Gorsky parameter is $S>0.9$). The high value of $S$ produced the necessary conditions for a manifestation of structural instability of the investigated compounds with $C$-15 structure.[13]

Figures 1 and 2 show the temperature dependences of the parameters of crystal lattices and of the relative resistances of the comporids $ZrV_2$ and $HfV_2$.[1] At relatively high temperatures, the plots of $a(T)$ and $\rho(T)$ are almost linear, but at temperatures ~157 K ($ZrV_2$) and ~120 K ($HfV_2$) anomalies appeared on the plots of the temperature dependences of the lattice parameters and of the resistance. The crystal-lattice parameter of $HfV_2$ began to increase slightly, while the parameter $ZrV_2$ decreased quite abruptly. For both compounds, a noticeable change was observed in the temperature dependences of the electric resistance, leading to its further drop in temperature to the appearance of minima on the $R(T)$ curves. We note that these anomalies were not accompanied by noticeable changes of the shapes of the diffraction lines of the investigated compounds. At temperatures $T_m = 80.0 \pm 2.0$ K for $ZrV_2$ and $T_m = 100.0 \pm 0.5$ K for $HfV_2$ a lowering of the symmetry of the cubic crystal lattice of $C$-15 type was observed, to tetragonal ($HfV_2$, Ref. 3) or rhombohedral ($ZrV_2$), and clearly pronounced maxima appeared on the $R(T)$ curves.

Judging from the character of the change of the crystal structure of the investigated compounds, $T_m$ exhibits all attributes of first-order phase transitions–a change

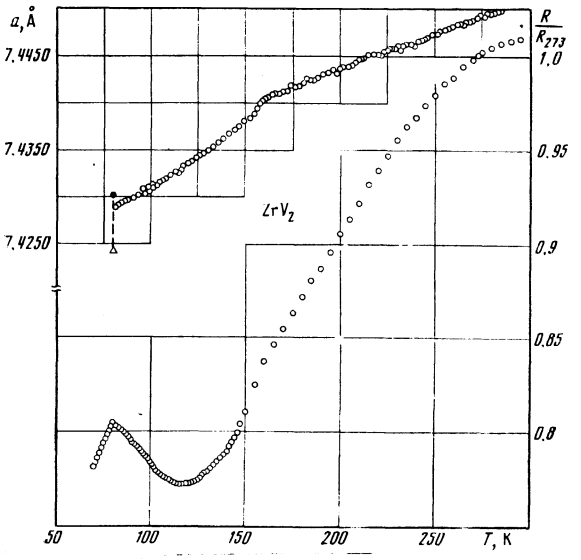


FIG. 1. Temperature dependence of the relative electric resistance ($R/R_{273}$) and of the crystal-lattice parameters of the compound $ZrV_2$: ○—$a_{cub}$, ●—$a_{hex}/\sqrt{2}$, △—$c_{hex}/\sqrt{3}$ (the rhombohedral lattice of the low-temperature magnification of $ZrV_2$ is described in terms of hexagonal axes.)

in the symmetry of the lattice and a jump in the atomic volume ($\Delta V/V$ amounts to ~$10^{-4}$ for $ZrV_2$ and ~$10^{-3}$ for $HfV_2$). A change in the slope of the $a(T)$ curves of the investigated compounds in the vicinity of the "high-temperature anomalies" points to the presence of a "jump" in the coefficient of thermal expansion–of the second derivative of the thermodynamic potentials, which is typical of continuous phase transitions (second-order transitions).

The assumption of a successive occurrence of two phase transitions–of second and first order–leading to loss of stability of crystal lattices of superconducting compounds with $C$-15 structure, agrees also with the character of the temperature dependences of the elec-

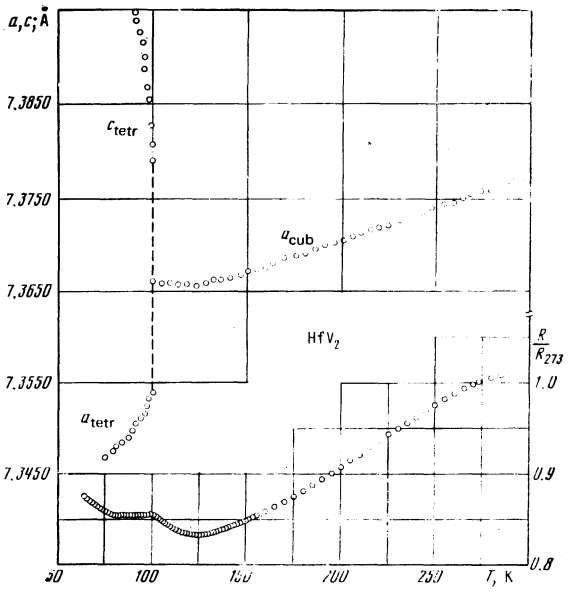


FIG. 2. Temperature dependence of the relative electric resistance and of the parameters of the crystal lattice of $HfV_2$.

tric resistance of the compounds $ZrV_2$ and $HfV_2$. Actually, at the temperature of the proposed phase transition of second-order there appears an additional contribution to the resistance, obviously due to the change in the number of carriers.[12] (The appearance of this contribution cannot be attributed to formation of nuclei of a high-temperature phase,[6] for in that case one would expect a smearing of the diffraction lines, something not observed in the experiment, in addition, this mechanism would not ensure the appearance of anomalies in the temperature dependences of the lattice parameters). When the temperature is lowered this contribution to the electric resistance increases, leading in final analysis to an inflection of the $R(T)$ curves. On the other hand, the presence on the $R(T)$ curves of a maximum having a position and shape that incidentally depend noticeably on the direction and rate of change of the temperature can be connected with the abrupt change of the kinetic properties of the investigated compounds when the initial cubic lattice is transformed into tetragonal or rhombohedral at the point of the first-order phase transition ($T_m$).

The notions developed here concerning the loss of stability of crystal lattices of superconducting compounds with $C$-15 structure as a result of a consecutive occurence of two phase transitions do not contradict the prevailing point of view, according to which the cause of the structural instability of this class of superconductors is a change in the electronic energy spectrum.[3,4,7,12] The point is that the space group $O_h^7 - Fd3m$ to which a lattice of $C$-15 type belongs contains nontrivial translations, and this leads to a double degeneracy of the electronic levels at the boundary of the Brillouin zone at the point $X$ with coordinates $(0, 0, 2\pi/a)$ and to a linear dispersion law.[15] If ther Fermi surface passes near the point $X$, the degeneracy is lifted, and it is this which causes the anomalous behavior of the electronic and lattice properties.[16] It appears that the described situation can take place in the investigated compounds at temperatures corresponding to second-order phase transitions. The appearance of a gap in the energy spectrum at the point $X$ can lead, with further decrease of temperature, to the turning on of a structural-instability mechanism at the points of the first-order phase transition ($T_m$) of the compounds $ZrV_2$ and $HfV_2$. Unfortunately, direct investigations of the electronic structure of these compounds have not been made.

The discrepancies in the temperature and in the "order" of the phase transition in superconductors with $C$-15 structure, as obtained by different investigations, may be due to the fact that in the experiments they registered different phase transitions, of second or first order, depending on whether the investigated microscopic property was maximally sensitive to the electronic or lattice changes. Nor can the possibility be excluded of a situation wherein only a "high-temperature" phase transition, connected in accordance with the concepts developed here with a change in the electronic spectrum, takes place in the compounds with $C$-15 structure, whereas the structural transformation initiated by this change does not have time to be realized. (Anomalies of vaious properties of $ZrV_2$ and $HfV_2$ and of ternary compounds with $C$-15 structure, not accompanied by any distortions of the crystal lattice, were noted in the literature a number of times[4,7,9,11]).

[1)]The results of the structural investigations of the $HfV_2$ compound (upper curve in Fig. 2) were obtained earlier[3] and are given here for convenience.


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