1) In Formula (1), V is the common part of the volumes V_1 and V_2.

2) The quantity $2L(1-\cos(\theta/2))$ has the meaning of the maximum difference between the paths of the singly and doubly scattered light.

3) The coefficients I_β^α at $h\neq 0$ will be designated by $I_\beta^\alpha(h)$, and at $h=0$ we shall omit the argument.

[1] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 60, 3359 (1974).
[2] E. L. Lakoza and A. V. Chalyĭ, Zh. Eksp. Teor. Fiz. 67, 1050 (1974) [Sov. Phys. JETP 40, 521 (1974)].
[3] L. V. Adzhemyan, L. Ts. Adzhemyan, L. A. Zubkov, and V. P. Romanov, Pis'ma Zh. Eksp. Teor. Fiz. 22, 11 (1975) [JETP Lett. 22, 5 (1975)].
[4] L. A. Reith and H. L. Swinney, Phys. Rev. A 12, 1094 (1975).
[5] D. Beysens and G. Zalczer, Opt. Commun. 26, 172 (1978).
[6] A. J. Bray and R. F. Chang, Phys. Rev. A 12, 2594 (1975).
[7] L. A. Reith and H. L. Swinney, Opt. Commun. 17, 111 (1976).
[8] I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Scattering of Light), Nauka, Moscow, 1965 [Plenum, (1968)].
[9] V. G. Puglielli and N. C. Ford, Jr., Phys. Rev. Lett. 25, 143 (1970).
[10] M. A. Anisimov, A. M. Evtyushenkov, Yu. F. Kiyachenko, and I. K. Yudin, Pis'ma Zh. Eksp. Teor. Fiz. 20, 378 (1974) [JETP Lett. 20, 176 (1974)].
[11] M. A. Anisimov, A. T. Berestov, V. Ya. Voronov, Yu. F. Kiyachenko, B. A. Koval'chuk, V. M. Malyshev, and V. A. Smirnov, Zh. Eksp. Teor. Fiz. 76, 1661 (1979) [Sov. Phys. JETP 49, 844 (1979)].
[12] M. Giglio and G. B. Benedek, Phys. Rev. Lett. 23, 1145 (1969).
[13] B. Chu, Ber. Bunsenges. Phys. Chem. 76, 202 (1972).

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Properties of the normal state and superconductivity in the Laves phases of $V_2Hf_{1-x}Zr_x$

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The superconductivity transition temperatures T_c, the temperature dependences of the magnetic susceptibility χ, and the heat capacity C_p of $V_2Hf_{1-x}Zr_x$ alloys ($0\leq x\leq 1$) are measured. In a narrow concentration range ($0.3\leq x\leq 0.4$) in which T_c attains its maximum and the structural transition temperature T_M is minimal, the transition entropy changes drastically from ~2 J/mole-K (alloys closer to V_2Hf) to 5.5 J/mole-K (alloys closer to V_2Zr). This corresponds to a change in the nature of the structural instability. The highest values of $\chi(T)$ are attained at temperatures that exceed T_M somewhat. They are the same for all values of x and are equal to 3.8×10^{-4} emu/g-atom. On the assumption that the orbital contribution is constant, it is concluded that the effective density of the electron states plays the decisive role in the onset of the structural transition. The low-temperature phase is characterized by a narrow (~500 K) minimum in the energy dependence of the state density. An analysis of the high-temperature entropy shows that lattice instability is accompanied by anharmonicity effects that manifest themselves in an appreciable decrease of the geometric mean phonon-spectrum frequency during cooling. It is suggested that the anharmonicity is due to electron contributions to the lattice dynamics.

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INTRODUCTION

Alloys based on the compounds V_2Hf and V_2Zr with C-15 structure have superconducting transition temperatures T_c up to 10 K.[1] The high values of the critical field $H_{c2}(4.2\text{ K})\approx 230$ kOe,[1] the increased endurance under irradiation,[2] and the lower formation temperatures[3] make them attractive in technical applications.

These isostructural and isoelectronic ($Z=4.67$ electrons per atom) compounds undergo at temperatures close to 100 K first-order phase transitions from the high-temperature cubic modifications into an orthorhombic (V_2Hf, Ref. 4) or an rhombohedral (V_2Zr, Ref. 5) low-temperature phase. X-ray structure investigations[6] reveal the presence of small but reliably measurable jumps of the lattice parameters at the structural-transition temperature, but the temperature dependences of such quantities as the resistivity or the specific magnetic susceptibility[7] do not exhibit the discontinuities typical of first-order transitions.

A correlation is observed between the superconducting and structural transitions T_c and T_m (the minimum of T_m corresponds to a maximum of T_s). This correlation seems to attest to a close connection between the superconductivity of the $V_2Hf_{1-x}Zr_x$ phases and the behavior of their lattice properties. From this point of view it is of interest to ascertain how the superconducting characteristics of the $V_2Hf_{1-x}Zr_x$ compounds depend on the properties in the normal state [such as the electronic state density at the Fermi level $N(E_F)$, the characteristic phonon frequencies $\tilde{\omega}_s$, and others].

The properties of the compounds V_2Hf and V_2Zr are the subject of a large number of papers (see, e.g., the bibliography in Ref. 8), but alloys on their basis have so far not been extensively investigated.

We have undertaken a measurement of the temperature dependences of the magnetic susceptibility of a number of samples of the quasibinary tie line $V_2Hf - V_2Zr$ for the purpose of determining the parameters of the electron and phonon spectra. These measurements make it possible to obtain information on the values of $N(E_F)$ and $\tilde{\omega}_s$ and reveal in a number of cases[9,10] the temperature-dependent contributions made to the electron-phonon interaction to the lattice dynamics. Since the lattice properties depend on the preparation conditions, the heat capacity and susceptibility were measured for the same samples prepared under identical conditions.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The initial components of the alloys were hafnium iodide zirconium iodide (metallic-impurity concentration on the order of $10^{-4} - 10^{-5}\%$) and electrolytic vanadium of brand VEL-1 (total impurity content not more than 0.1%). The vanadium was first outgassed by heating and melting in a vacuum of 10^{-5} Torr. The chopped-up and etched components were wrapped in foil of the same vanadium and melted in an atmosphere of spectrally pure argon ($p = 0.8$ atm) in the suspended state, and then poured into water-cooled copper molds (ingot weight 10 g). All the samples were heat treated at 1200°C for 120 hours in a TVV-4 furnace. The microstructure of the cast samples, which were close in composition to V_2Hf, was practically single-phase, while that of samples close to V_2Zr was quite complex, apparently indicating that they were subjected to a nonequilibrium peritectic reaction.[3] After heat treatment, metallographic examinations of all samples revealed in the main a single-phase structure with small amounts (up to 5%) of precipitates along the grain boundaries and sparsely distributed platelets of an extraneous phase inside the grains. A study of the concentration profile by x-ray microanalysis has shown the components to be uniformly distributed in the matrix, and the precipitate to be an α-solution of the components in vanadium.

The superconducting transition temperature was measured by an inductive method with absolute accuracy 0.1 K. In different sections of the heat-treated ingot, T_c varies insignificantly for alloys close in composition to V_2Hf (±0.2 K), and more substantially for alloys close to V_2Zr (±0.6 K).

The values of T_c of annealed samples, averaged over measurements of three or four pieces of each composition, are shown by the continuous line in Fig. 1. The circles mark the values of T_c of samples whose susceptibility and heat capacity were measured. There is a noticeable singularity in the concentration dependence of T_c near the composition with $x = 0.35$.

A number of V_2Zr samples had, besides a T_c close to 7.7 K, also a step of much smaller height than the main one at temperatures 8.5 – 8.9 K. An estimate of T_c from the measured values of the heat capacity (from the temperature of the midpoint of the heat-capacity jump in the superconducting transition) yields results identical with those obtained by the inductive method. The half-width of the superconducting transition, as obtained from the heat-capacity data, is 0.05 – 0.2 K.

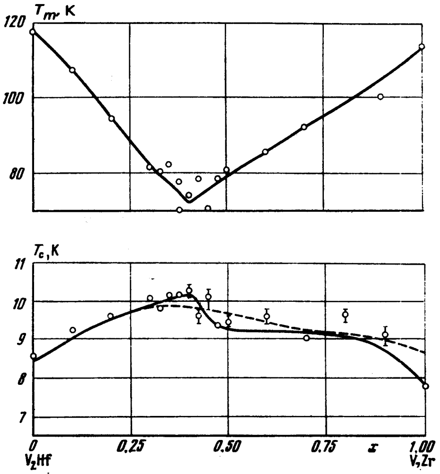

FIG. 1. Dependence of T_M (upper plot) and of T_C on the composition. Solid line—heat treated samples, dashed—cast. The vertical lines mark the width of the transition.

The cast samples with compositions close to $V_2Hf_{0.2}Zr_{0.8}$ revealed the presence of several transitions within a range of 1 K. The maximum change of the magnetic moment occurs at the transition with the lowest temperature. The averaged values of T_c of cast samples are shown dashed in Fig. 1.

Measurements of the temperature dependence of the magnetic susceptibility $\chi(T)$ in the interval from T_c to 280 K were made by the Faraday method with a string magnetometer similar to that described in Ref. 11. The sample temperature was measured with a KG thermometer produced by the Institute of Semiconductor Physics of the Ukrainian Academy of Science, placed together with the sample in a copper thermostat. The magnetometer was calibrated against high-purity molybdenum ($\rho(300\text{K})/\rho(4.2\text{ K}) \approx 2 \cdot 10^4$). It was assumed that $\chi_{Mo}(273\text{ K}) = 0.82 \cdot 10^{-6}$ emu/g-atom. The absolute error in the measurement of the susceptibility, ±2.5%, was determined by the inaccuracy of the placement of the sample in the magnetic field of the superconducting solenoid; the relative accuracy (in one experiment without change of sample) was 0.1%. The rate of change of temperature was usually 1–2 K per minute.

The heat capacity was measured for the samples whose magnetic susceptibility was investigated. Since the sample mass did not exceed 0.8 g, C_p was measured by a microcalorimetric method based on an exact comparison of the heat fluxes to the investigated sample and to a standard having a well-known heat capacity.[12] The measurements were made at a heating rate 0.5 K per minute. The measurement error of C_p was 2–3% in the 4– 0 K interval and decreased to 1–0.5% above 10 K.

MEASUREMENT RESULTS AND THEIR ANALYSIS

The $\chi(T)$ plots of all samples are similar: when the temperature is lowered, χ first increases, reaches a gently sloping maximum, and then drops off somewhat. The structural transition is accompanied by a steep drop of χ, followed by a nearly quadratic decrease to the values $\chi(0)$. Figure 2 shows several typical plots of (T). Measurements with the sample heated and cooled show a hysteresis of (T) amounting to 6–25 K near the structural transition. The susceptibility of some of the samples decreases jumpwise in the vicinity of the structural transition. The susceptibility jump and the presence of hysteresis offer unequivocal evidence that the transition is of first order.

The characteristic parameters of the $\chi(T)$ functions can be taken to be the maximum susceptibility χ_{max}, the susceptibility $\chi(0)$ extrapolated to 0 K, and the temperature T_m of the maximum of the derivative $\partial\chi/\partial T$. These parameters are shown in Figs. 1 and 5 (see below). The presented values of T_m correspond to $\chi(T)$ of samples in the course of heating. The sample with composition $V_2Hf_{0.625}Zr_{0.375}$ shows two sections with large changes of $\chi(T)$, corresponding to the two points shown in Fig. 1 at this composition.

The low-temperature ($T < 60$ K) section of $\chi(T)$ was plotted in the coordinates $\chi(T)$ and T^2, with the quadratic term separated, $\chi(T) = \chi(0) + A'T^2$. The coefficient A' ranges from 0.35×10^{-8} emu/g-atom-K^2 for alloys rich in Hf to 0.16×10^{-8} emu/g-atom-K^2 for alloys rich in Zr.

Typical plots of the heat capacity against temperature are shown in Figs. 3 and 4. The heat-capacity peak temperature coincide with the maximum temperature T_m of the derivative $\partial\chi/\partial T$. (Two respective peaks were observed in the $V_2Hf_{0.625}Zr_{0.375}$ sample.) The heat capacity in the considered alloys has a non-Debye behavior even at temperatures slightly above T_c (Fig. 4). To analyze the low-temperature section from T_c to 15 K, the heat capacity was approximated by the power series

$$C_p(T)=C_E+C_L=\gamma_0T+\alpha T^3+\beta T^5+\delta T^7, \tag{1}$$

where C_E and C_L are respectively the contributions of conduction and lattice electrons, α is a coefficient that determines the Debye temperature $\Theta_0{}^c$ in the limit as $T \to 0$, and β and δ are coefficients that characterized from the Debye "T^3 law"

$$\gamma_0=\lim_{T\to 0}(C_E/T)={}^1/_3\pi^2k^2N_{band}(E_F)(1+\lambda_0)\equiv\gamma_{band}(1+\lambda_0) \tag{2}$$

(k is Boltzmann's constant, and λ_0 is the electron-phonon interaction constant).

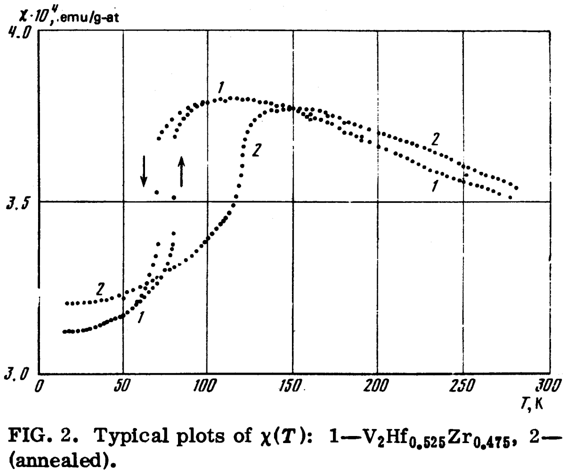

FIG. 2. Typical plots of $\chi(T)$: 1—$V_2Hf_{0.525}Zr_{0.475}$, 2—V_2Zr (annealed).

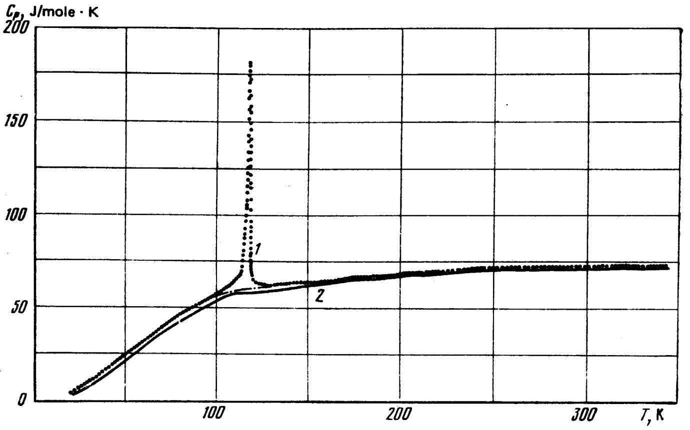

FIG. 3. Heat capacity of the compound V_2Zr: 1—annealed sample, 2—cast. The dash-dot curve shows the "basic" values of the annealed sample in the region of the structural transition.

To determine the coefficients in (1) we used as a restriction the condition that the entropy be continuous at the superconducting transition point:

$$\int_0^{T_0>T_c}\frac{C_S}{T}dT=S(T_0)=\gamma_0T_0+\frac{1}{3}\alpha T_0{}^3+\frac{1}{5}\beta T_0{}^5+\frac{1}{7}\delta T_0{}^7, \tag{3}$$

where C_S is the heat capacity in the superconducting state.

The results of the analysis of the low-temperature heat capacity of the alloys are given in Fig. 5 and in the table. The main result is that the electronic heat-capacity coefficient γ_0 is maximal and the Debye temperatures Θ_0^c are minimal in alloys having the maximum T_c.

Taking into account the MacMillan formula[13]

$$T_c=\frac{\Theta_0{}^c}{1.45}\exp\left[-\frac{1.04(1+\lambda_0)}{\lambda_0-\mu^*(1+0.62\lambda_0)}\right], \tag{4}$$

we calculated from the experimental values of T_c and Θ_0^c the electron-phonon interaction constants λ_0. The parameter μ^* of the screened Coulomb interaction was assumed to the same for all alloys: $\mu^* = 0.13$.

Starting from the values of λ_0 and γ_0 and using (2),

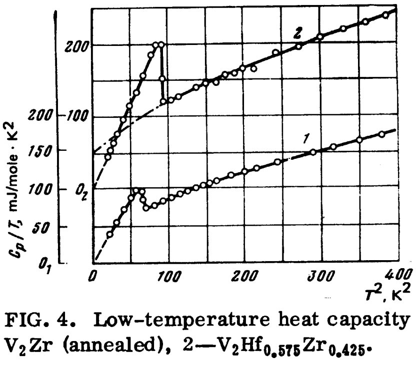

FIG. 4. Low-temperature heat capacity of the compounds: 1—V_2Zr (annealed), 2—$V_2Hf_{0.575}Zr_{0.425}$.

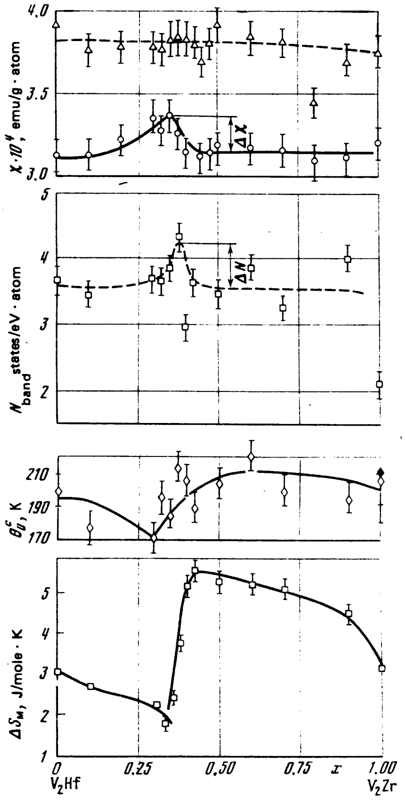

FIG. 5. Concentration dependences of the maximal (△) and low-temperature (○) values of the susceptibility, of the state density $N_{band}(E_F)$, of the Debye temperature Θ_0^c (♦—cast sample), and of the transition entropy ΔS_m.

we determined also the values $N_{band}(E_F)$ of the "renormalized" state density on the Fermi level in the limit as $T\rightarrow 0$. The values of λ_0 and $N_{band}(E_F)$ are listed in the table.

Spread-out phase transitions (over an interval 30–50 K), similar in the form of their anomalies to second-order heat-capacity transition, take place in $V_2Hf_{1-x}Zr_x$ alloys at temperatures close to T_m. As already noted, however, the presence of temperature hysteresis and of discontinuities in the susceptibility at these temperatures points to a first-order transition.

To determine the energy behavior of the transitions we calculated the changes they produce in the entropy

$$\Delta S_m=\int_{T_1}^{T_2}\Delta C(T)\,d\ln T,$$

where $\Delta C(T)$ is the change of the heat capacity in the interval T_1-T_2 relative to the "basic" values. It follows from the obtained data (see Fig. 5) that near the composition with $x=0.35$, where the minima of T_m and ΔS_m are reached, the character of the restructuring changes. In a narrow concentration region ($x=0.35-0.40$) the energy parameter of the transition ΔS_m, which is connected with the lattice distortion, changes from ~2 J/mole-K (alloys on the V_2Hf side) to 5.5 J/mole-K (alloys on the V_2Zr side). This agrees with the results of direct structural investigations,[4,5] according to which the low-temperature phase of V_2Hf has an orthorhombic lattice with a distortion parameter of only 10^{-3}, whereas V_2Zr has below T_m a rhombohedral structure whose distortion parameter is smaller by about one order of magnitude. Judging from the concentration dependence of ΔS_m we can conclude that the $V_2Hf_{1-x}Zr_x$ alloys with $x<0.35$ have the same low-temperature structure as V_2Hf, while at $x>0.40$ their structure is analogous to V_2Zr. Unfortunately, the lack of direct measurements of the structure of the alloys with $x=0.375$ does not indicate whether the presence of two singularities of $C_p(T)$ and $\chi(T)$ is due to a succession of different structural transitions of the entire volume or to transitions of two regions of the sample at different temperature.

TABLE I. Parameters of the compounds $V_2Hf_{1-x}Zr_x$.

x	γ_0, mJ/g-at-K^2	Θ_0^c, K	λ_0	$N_{band}(E_F)$ states/eV-at	ΔS_m, J/mole-K	$-\frac{A}{3R}$, 10^{-4} K^{-1}
0.0	16.7	199.0	0.92	3.7	3.06	3.0
0.1	16.3	177.0	1.02	3.4	2.65	3.4
0.3	18.3	170.5	1.11	3.7	2.21	3.0
0.325	17.3	195.5	1.02	3.6	1.76	
0.350	18.7	184.1	1.06	3.8	2.37	3.4
0.375	20.0	213.4	0.97	4.3	3.74*	
0.4	13.5	205.7	0.96	2.9	5.11	3.1
0.425	17.2	189.0	1.01	3.6	5.49	
0.50	15.8	204.0	0.94	3.5	5.18	3.2
0.6	17.3	221.0	0.89	3.9	5.15	
0.7	15.0	199.0	0.95	3.3	5.01	3.2
0.9	18.7	194.0	0.96	4.0	4.40	3.1
1.0 (annealed)	10.0	207.5	0.88	2.3	3.07	2.7
1.0 (cast)	9.7	210.3	0.90	2.2	–	1.6

*Transition entropy corresponding to both C_p peaks.

The effects of the structural instability in the $V_2Hf_{1-x}Zr_x$ compounds depends strongly on the metallurgical state of the samples, and in particular on the heat-treatment conditions.[14,15] This seems to explain the difference between the values of ΔS_m obtained in Ref. 16 and in the present paper. This dependence the properties of the compounds on the metallurgical state is clearly illustrated with V_2Zr as an example. In Fig. 3 are compared the measured heat capacities of annealed and cast (quenched) samples. Whereas the $C_p(T)$ curve of the annealed sample has a sharp peak at 118 K, only a small change of the slope can be observed at this temperature on the $C_p(T)$ curve of the cast sample. This result indicates that there is practically no phase transition in the cast sample (if this transition does occur, it affects not more than 3% of the sample volume). This behavior of cast and annealed V_2Zr samples agrees with the assumption[15] that in rapidly cooled V_2Zr samples the cubic phase is preserved all the way to T_c.

DISCUSSION OF RESULTS

The main contributions to the magnetic susceptibilities of transition metals and of alloys on their based are the orbital and the spin ones (Pauli paramagnetism)[17]:

$$\chi=\chi_{orb}+\chi_P. \tag{5}$$

The spin part is proportional to the state density on the Fermi level

$$\chi_P(0)=2\mu_B^2N_{band}(E_F)/(1-\xi) \tag{6}$$

(μ_B is the Bohr magneton and ξ is the exchange enhancement factor). It is customary to estimate the orbital paramagnetism from the expression

$$\chi_{orb} \approx 2\mu_B^2 n(10-n)/\Delta, \tag{7}$$

where n is the number of d electrons and Δ is the energy width of the d band. The investigated alloys have equal numbers (4.67) of electrons per atom, and the lattice parameters of the quasibinary tie line change little (7.38 and 7.44 Å for V_2Hf and V_2Zr respectively). χ_{orb} is therefore expected to depend little on the concentration.

Examination of the crystal structure of the investigated compounds shows that the distance between the nearest V atoms in V_2Hf ($d_{V-V} = 2.61$ Å) is very close to the distances in metallic[18] V ($d = 2.62$ Å) and the distances between the nearest Hf atoms ($d_{Hf-Hf} = 3.19$ Å) practically coincide with those in metallic Hf ($d = 3.195$ Å). The V and Hf atoms in a C-15 structure make little contact with each other, since $d_{V-Hf} = 3.06\ \text{Å} > \frac{1}{2}(d_{V-V} + d_{Hf-Hf}) = 2.9$ Å. It can therefore be assumed that the overlap of the d-electron wave functions in a C-15 structure differs little from the overlap in the pure components, and the orbital contribution to the susceptibility can be close to the sum of the orbital contributions of the components. Since different methods[17] yield $\chi_{orb,V} = 1.8 \cdot 10^{-4}$, $\chi_{orb,Hf} = (0.4 - 1.0) \cdot 10^{-4}$, and $\chi_{orb,Zr} = (0.7 - 1.1) \cdot 10^{-4}$ emu/g-atom, it follows that $\frac{2}{3}\chi_{orb,V} + \frac{1}{3}\chi_{orb,Hf-Zr} = (1.3 - 1.6) \cdot 10^{-4}$ emu/g-atom.

Estimates of χ_{orb} from the experimental data are obtained from the correspondence of the values of $N_{band}(E_F)$ shown in Fig. 5 and obtained from measurements of the heat capacity, with the values of the susceptibility $\chi(0)$ obtained at 0 K. Substituting $N_{band}(E_F)$ in (6) and assuming $\xi \ll 1$, we obtain from (5) $\chi_{orb} \approx 2.0 \times 10^{-4}$ emu/g-atom, which does not differ greatly from the value obtained by simple summation of the contributions of the components.

The assumption $\xi \ll 1$ is justified by the fact that the investigated alloys are superconductors with sufficiently high T_c, for which the exchange interaction effects that lead to parallel alignment of the electron spins should be small.

It is seen from the concentration dependence of $\chi(0)$ (Fig. 5) that a maximum exists in the vicinity of the composition with $x = 0.35$. Attributing the increase of $\chi(0)$ in this vicinity to an increase of χ_p in proportion to $N_{band}(E_F)$ ($\Delta\chi_p = 2\mu_B^2 \Delta N$), we arrive at the conclusion that the concentration dependence of $N_{band}(E_F)$ should have a maximum at these concentrations. The dashed plot of $N_{band}(E_F)$ in Fig. 5 is drawn with just this circumstance taken into account. The deviation of the point for the composition $V_2Hf_{0.6}Zr_{0.4}$ from the general law is due in our opinion to a random experimental error.

Both components of the magnetic susceptibility in (5) can be temperature dependent. Calculations[19] show, however, that even in the case of energy bands with narrow peaks in the $N(E_F)$ dependence the change of the orbital contribution with temperature (from 10 to 300 K) is much less than the change of the spin component. All the changes of the susceptibility with temperature are therefore usually attributed to the change of χ_p.

The temperature dependence of $\chi_p(T)$ is described in first order in T^2 by the expansion[17]

$$\chi_p(T) = -2\mu_B^2 \int_0^\infty N_{band}(E) \frac{\partial f}{\partial E} dE \approx 2\mu_B^2 N_{band}(E_{F_0}) \left\{ 1 + \frac{\pi^2}{6} \left[\frac{N''}{N} - \left(\frac{N'}{N} \right)^2 \right] k^2 T^2 \right\}, \tag{8}$$

where N' and N'' are the derivatives of $N_{band}(E)$ with respect to energy at $E = E_{F_0}$. The growth of the susceptibility with temperature is therefore connected with the location of E_{F_0} near a minimum of $N_{band}(E)$. Assuming

$$N_{band}(E) = N_{band}(E_{F_0}) \{1 + (E - E_{F_0})^2 / E_0^2\},$$

we have

$$\frac{\chi_p(T)}{\chi_p(0)} = 1 + \frac{\pi^2}{3} \frac{1}{E_0^2} k^2 T^2.$$

Using the experimentally determined values of $A' = \partial\chi/\partial T^2$ (see above), we obtain $E_0 = (5 - 3.4) \cdot 10^2$ K (the larger value corresponds to samples richer in zirconium). Thus, the low-temperature phase of the investigated alloys is characterized by the presence of a narrow minimum of $N_{band}(E)$ near the Fermi level.

In the cubic phase at high temperatures [above the temperature of the maximum of $\chi(T)$] the susceptibility decreases with increasing temperature. This situation is more complicated from the point of view of choosing the model of the $N_{band}(E)$ dependence. It is known that the inequality $\partial\chi/\partial T < 0$ can be brought about by two circumstances: location of the Fermi level near a maximum of $N_{band}(E)$ [as follows from (8)] or near the region where $N_{band}(E)$ decreases sharply. The first case does not lend itself to a simple analysis, since $\chi(T)$ falls off much more slowly than quadratically at high temperatures. The second case was considered for C-15 compounds in Ref. 20. In our opinion the small temperature interval of the measurements and the large number of parameters needed for the fit[20] does not make it possible at present to determine unambiguously the form of the electron spectrum in the cubic phase.

Since the spin part of the susceptibility is determined by the value of $N_{band}(E)$ averaged over the kT-vicinity of the Fermi level (8), the growth of $\chi(T)$ with decreasing temperature is evidence of an increase of the effective state density with decreasing temperature. The maximum values of $\chi(T)$ are the same for alloys within the limits of the measurement errors (Fig. 5). It appears that this fact points to a decisive role of the state density in the onset of the structural transition: when a definite density 5.6 states/eV-g-atom is reached (assuming $\chi_{orb} = 2.0 \cdot 10^{-4}$ emu/g-atom), the cubic phase becomes unstable. It is probable that microregions of the low-temperature phase are initially produced in the cubic phase and lower slightly the susceptibility when the structural transition temperature is approached from above.

The difference between the magnetic susceptibilities of the high-temperature and low-temperature phases (the difference between the values of χ_{max} and $\chi(0)$, Fig. 5), which is proportional to the difference of the state density, is minimal in the concentration region $x = 0.35$. This minimum corresponds to a minimum of the difference ΔS_m between the entropies of the high- and low-temperature phases (Fig. 5), and also to the minimum of the difference between the volumes of the unit cells before and after the transition.[21] Corresponding to this minimum difference between the properties are the maximum of T_c and the minimum of T_m. It appears that the C-15 cubic structure is more favorable for obtaining high T_c than the low-temperature phases. This conclusion is confirmed also by the higher (8.7 K) value of T_c in cast (cubic) V_2Zr samples compared with T_c of annealed samples (7.9 K).

Proceeding to a discussion of the results of the measurement of C_p, we note that the high-temperature heat capacity does not reach its classical value (≈74.83 J/mole-K). This is obviously evidence of large anharmonic contributions to the heat capacities of the investigated materials. Information on the anharmonicity of the lattice vibrations, particularly on the temperature dependence of the frequencies of the normal modes, can be obtained by analyzing the high-temperature thermodynamic properties expressed in terms of the moments of the frequency distribution function $F(\omega)$. The measurements of the heat capacity can yield the "zeroth" moment of the spectrum of the geometric mean of the phonon frequency[22]:

$$\omega_g=\left(\prod_{s=1}^{3N}\omega_s\right)^{1/3N}=\exp\left[\frac{1}{3N}\int\limits_0^{\omega_{max}}F(\omega)\ln\omega\,d\omega\right].$$

The zeroth moment is the leading moment of the expansion of the lattice vibrational entropy in the reciprocal powers of the temperature, which converges[23] at $T > \Theta_0{}^c/2\pi$:

$$S_L(T)=3Nk\left[1-\ln\frac{\hbar\omega_g(T)}{kT}-\sum_{n=1}^{\infty}(-1)^n\frac{2n-1}{2n(2n)!}B_{2n}\left(\frac{\hbar}{kT}\right)^{2n}\langle\omega^{2n}\rangle\right], \tag{9}$$

where B_n are Bernoulli numbers and $\langle\omega^{2n}\rangle$ are the even moments of the frequency distribution.

The corresponding expansion for the heat capacity $C_p=T(\partial S/\partial T)_p$ (the Thirring-Stern series) is

$$C_L=3Nk\left[1+\sum_{n=1}^{\infty}(-1)^n\frac{2n-1}{2n!}B_{2n}\left(\frac{\hbar}{kT}\right)^{2n}\langle\omega^{2n}\rangle\right]+AT, \tag{10}$$

where AT is the anharmonic component of the heat capacity at constant pressure,

$$\frac{A}{3Nk}=-\frac{\partial\ln\omega_g(T)}{\partial T}=-\frac{1}{3N}\sum_{s=1}^{3N}\frac{1}{\omega_s}\left(\frac{\partial\omega_s}{\partial T}\right)_p,$$

is the temperature-dependent shift of the geometric mean of the frequency. The main difficulty in the determination of the function $\omega_g(T)$ lies in obtaining an adequate estimate of the conduction-electron entropy:

$$S_E(T)=\int\limits_0^T\gamma_{\text{band}}[1+\lambda(T')]dT'=\int\limits_0^T\gamma_{\text{band}}dT'+\int\limits_0^T\gamma_{\text{band}}\lambda(T')dT', \tag{11}$$

[$\lambda(T)$ is a parameter that describes the contribution to the heat capacity from the electron-phonon interaction, $\lim\lambda(T)=\lambda_0$ as $T\to 0$]. At high temperatures ($T>\Theta_0^c$) the contribution to the entropy from the electron-phonon interaction [the second integral in (11)] vanishes.[24,25] The variation of the coefficient $\gamma_{\text{band}}\sim N_{\text{band}}(E_F)$ with temperature is due mainly to the thermal broadening of the Fermi distribution and to the shift of the Fermi level E_F, which is needed to maintain the number of carriers constant. In metals such as $V_2Hf_{1-x}Zr_x$, where a strong temperature dependence of the paramagnetic susceptibility is observed, one can use as a limitation on the form of $\chi_{\text{band}}(T)$ the function $\chi_p(T)=\chi(T)-\chi_{\text{orb}}$.

We have calculated the function $\omega_g(T)$ for the alloys $V_2Hf_{1-x}Zr_x$, using the assumption that the orbital contribution to $\chi(T)$ does not depend on the temperature or composition, and is equal to 2×10^{-4} emu/g-atom. The electron contribution to the entropy of the considered compounds is small (<7%) and, as shown with V_2Hf as an example,[10] the form of the function $\omega_g(T)$ does not change qualitatively, while the quantitative variations of the numerical values do not exceed 15% at all reasonable assumptions concerning the temperature dependence of $\gamma_{\text{band}}(T)$. The procedure of calculating $\omega_g(T)$ on the basis of the experimental data on $S_L(T)$ and the assumptions used in it are discussed in detail in Refs. 9 and 10. The temperature dependence of $_D(0) = 1.4\hbar\omega_g/k$ is plotted in Fig. 6. In view of the uncertainty in the estimate of $\gamma_{\text{band}}(T)$, the information obtained from the $\omega_g(T)$ curves is mainly qualitative in character. Nonetheless, within the framework of the assumptions made it can be stated that the coefficients $-A/3R$ (see the table) which describe the temperature softening of the average phonon frequencies are relatively large ($\sim3\times10^{-4}$ K^{-1}) in $V_2Hf_{1-x}Zr_x$ alloys. The effects of anharmonicity in the $V_2Hf_{1-x}Zr_x$ compounds are larger than in superconducting compounds with A-15 structure, where[9] $-A/3R\leq2.4\times10^{-4}$ K^{-1}. A noticeable temperature shift of the average phonon frequencies ($-A/3R=1.6\cdot10^{-4}$ K^{-1}) is observed also in the quenched V_2Zr alloys, which does not undergo a structural transition. The coefficient A obtained by us for the alloy V_2Hf agrees well with the estimate obtained in Ref. 10.

The temperature dependence of the characteristic lattice frequencies can be due to two causes: a substantial deviation of the real phonon spectrum from the Debye spectrum (owing to the presence of high-frequency phonon modes with $\omega_s > k\,\Theta_0{}^c/\hbar$), or as a result of the temperature dependence of the renormalization of the pho-

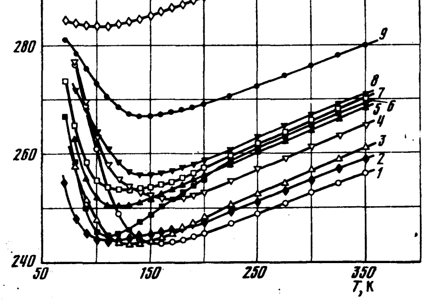

FIG. 6. Temperature dependence of the geometric-mean frequency ($\Theta_D(0)=1.4\hbar\omega_g/k$ of the compounds $V_2Hf_{1-x}Zr_x$: 1—$x=0$, 2—0.4, 3—0.1, 4—0.3, 5—0.5, 6—0.7, 7—0.35, 8—0.9, 9—x = 1.0 (annealed), 10—x=1.0 (cast).

non frequencies on account of electron-ion interaction. The phonon frequencies are determined by the screened Coulomb interaction of the ions, which depends in turn on the state of the electron subsystem, particularly on $N(E_F)$.

According to present-day concepts, the observed phonon frequencies are determined within the framework of an electron-ion Hamiltonian with Coulomb interaction of the electrons and ions, by the relation[26,27]

$$\omega^2(q,T)=\omega_0^2\left[1-\frac{g_0^2(q)\chi_0(q,T)}{1+V(q)\chi_0(q,T)}\right], \qquad (12)$$

where ω_0 is the unrenormalized frequency of the ion lattice, $g_0(q)$ is the matrix element of the interaction of the electrons with the unrenormalized ion oscillations, $V(q)$ is the direct Coulomb interaction of the electrons, and $\chi_0(q,T)$ is the static polarizability of the noninteracting electrons and is approximately proportional to $N(E_F)$.

If we represent $\chi_0(q,T)$ formally in the form $\chi_0(q,T)=\chi_p(T)c(q)$, where $c(q)$ is a function independent of temperature, then relation (12) can be rewritten in the form[10]

$$\omega^2(q,T)=\omega_0^2\{1-F[\chi_p(T)]\},$$

where $F(\chi_p)$ is a function that increases monotonically with χ_p.

The relation between $\omega_g^2(T)$ and $\chi(T)$ in the temperature region 120–350 K is illustrated for the investigated materials in Fig. 7. It is seen that within the limits of experimental errors the correlation between $\omega_g(T)$ and $\chi(T)$ does not depend on the composition or temperature. An increase of $\chi(T)$ with changing temperature for a given composition or an increase of $\chi(T)$ at fixed temperature with change of composition leads to the same value of the squared average frequency. This is obviously also evidence that in the cubic phase of the $V_2Hf_{1-x}Zr_x$ compounds the unrenormalized frequencies depend little on the composition.

The values of $\omega_g^2(T)$ for the quenched V_2Zr lie much higher than those for the annealed alloys and deviate from the general dependence. A correlation between the measured values of $\omega_g^2(T)$ and $\chi(T)$ was established earlier[10] for the alloys $V_2Hf_{1-x}Ta_x$.

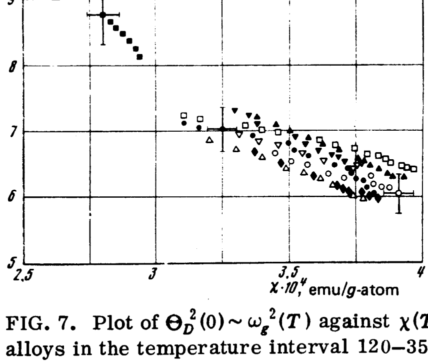

FIG. 7. Plot of $\Theta_D^2(0)\sim\omega_g^2(T)$ against $\chi(T)$ of the $V_2Hf_{1-x}Zr_x$ alloys in the temperature interval 120–350 K: ○—x = 0; △—0.1; ▽—0.3; □—0.35; ◆—0.4; ▲—0.5; ●—0.7; ▼—0.9; ■—x = 1.0 (cast).

Thus, the effects of anharmonicity (temperature softening of the phonon modes) in the superconducting compounds $V_2Hf_{1-x}Zr_x$ are due to the strong increase of the electron contribution to the phonon frequencies, a contribution proportional to the electron-ion potential and to the electronic (spin) susceptibility. (T) increases noticeably on cooling, and then the parameter $\{1-F(\chi_p)\}$, which characterizes the unstable phonon modes, decreases and approaches zero. At a certain critical value (corresponding to $\chi_c\approx 3.8\cdot 10^{-4}$ emu/g-atom, which is almost constant for all alloys), a restructuring of the system takes place and results in strains due to the development of a new phase. In the case V_2Zr alloy the interval of the variation of $\chi(T)$ with temperature is small and the value of χ itself is much less, so that no structural transition due to the instability of the cubic phase is realized in this alloy.

[1] K. Inoue and K. Tachikawa, J. Jpn. Inst. Metals **39**, 1266 (1975).
[2] B. S. Brown, J. W. Hafstrom, and I. E. Klippert, J. Appl. Phys. **48**, 1759 (1977).
[3] I. R. Finlayson and M. R. Khan, Appl. Phys. **17**, 165 (1978).
[4] A. C. Lawson and W. H. Zachariasen, Phys. Lett. A **38**, 1 (1972).
[5] D. E. Moncton, Solid State Commun. **13**, 1779 (1973).
[6] V. E. Ivanov, V. A. Finkel', and V. A. Pushkarev, Dokl. Akad. Nauk SSSR **228**, 119 (1976).
[7] V. M. Pan, I. E. Bulakh, A. L. Kasatkina, and A. D. Shevchenko, Fiz. Tverd. Tela (Leningrad) 20, 2487 (1978) [Sov. Phys. Solid State 20, 1437 (1978)].
[8] S. V. Vonsovskiĭ, Yu. A. Izyumov, and E. Z. Kurmaev, Sverkhprovodimost' perekhodnykh metallov, ikh splavov i soedineniĭ (Superconductivity of Transition Metals, Their Alloys, and Their Compounds), Naukå, 1977.
[9] G. S. Knapp, S. D. Bader, H. V. Gilbert, F. Y. Fradin, and T. E. Klippert, Phys. Rev. **B11**, 4331 (1975). G. S. Knapp, S. D. Bader, and Z. Fisk, Phys. Rev. **B13**, 3783 (1976).
[10] J. W. Hafstrom, G. S. Knapp, and A. T. Aldred, Phys. Rev. **B17**, 2892 (1978).
[11] N. E. Alekseevskiĭ, E. P. Krasnoperov, and V. G. Nazin, Dokl. Akad. Nauk SSSR **197**, 214 (1971).
[12] N. M. Gavrilov, V. M. Polovov, and R. R. Ponomareva, Prib. Tekh. Eksp. No. 5, 213 (1979).
[13] W. L. MacMillan, Phys. Rev. **167**, 331 (1968).
[14] M. Levinson, C. Zahradnick, R. Bergh, M. L. A. MacVicar, and J. Bostock, Phys. Rev. Lett. **41**, 899 (1978).
[15] V. A. Finkel' and V. A. Pushkarev, Zh. Eksp. Teor. Fiz. **73**, 2332 (1977) [Sov. Phys. JETP **46**, 1220 (1977)].
[16] Y. Kimura, Jpn. J. Appl. Phys. **16**, 517 (1977).
[17] E. V. Galoshina, Usp. Fiz. Nauk **113**, 105 (1974) [Sov. Phys. Usp. **17**, 345 (1974)].
[18] G. Schulze, Metal Physics (Russ. transl.), Mir, 1971, p. 424.
[19] E. Ehrenfreud, A. C. Gossard, and J. H. Wernick, Phys. Rev. **B4**, 2906 (1971).
[20] Y. Kimura, Phys. Status Solidi A **43**, K141 (1977).
[21] A. C. Lawson, Phys. Rev. **B17**, 1136 (1978).
[22] F. C. K. Hui and P. B. Allen, J. Phys. **C8**, 2923 (1976).
[23] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, Academic, 1963.
[24] G. Grimvall, J. Phys. Chem. Solids **29**, 1221 (1968).
[25] N. F. Masharov, Fiz. Tverd. Tela (Leningrad) **16**, 3306 (1974); **18**, 295 (1976) [Sov. Phys. Solid State **16**, 2147 (1975); **18**, 174 (1976)].
[26] S. K. Chan and V. Heine, J. Phys. **F3**, 795 (1973).
[27] E. G. Maksimov, Zh. Eksp. Teor. Fiz. **69**, 2236 (1975) [Sov. Phys. JETP **42**, 1138 (1975)].

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