Abstract—The heat capacity of Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ icosahedral quasicrystals and their amorphous counterparts is studied in the temperature range 1.5–500 K in order to establish a correlation between the short-range atomic order and the physical properties of these compounds. A comparison of the data made it possible to reveal changes in the vibrational spectra within the low- and high-energy ranges, as well as in the density of states, superconducting characteristics, electron–phonon interaction, and anharmonicity of the lattice thermal vibrations and to calculate the main average frequencies (moments) characterizing the vibrational spectra. The lower superconducting transition temperature $T_c$ of the quasicrystals as compared to that of the amorphous counterparts can be associated with the decrease in the density of states on the Fermi surface, the hardening of the phonon spectrum, and the weakening of the electron–phonon coupling.

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1. INTRODUCTION

Studies of lattice dynamics and thermodynamic, transport, and other properties of binary metallic systems, which can exist in both quasicrystalline and amorphous state, can provide a better understanding of the physical characteristics inherent in these states.

The unusual atomic structure of quasicrystals, with long-range atomic order realized in the absence of translational symmetry, and the disordered atomic structure of the amorphous phase, when no long-range order exists in the arrangement of atoms, have offered considerable possibilities for carrying out comparative studies of isostoichiometric compounds with different crystal structures.

The most complete and reliable information on the structure and dynamics of such systems can be gained in elastic and inelastic neutron scattering experiments; if no such information is available, however, studies of the temperature dependence of heat capacity over a wide temperature range can provide a wealth of representative data for a qualitative estimation of the integral parameters of the vibrational spectrum which characterize it within different frequency intervals.

Investigation of the temperature dependence of the heat capacity in the high-temperature range, combined with low-temperature measurements, permits one to derive the main integral characteristics of the vibrational spectrum, which offer a qualitative and quantitative insight into its major features.

There are publications dealing with structural studies of binary metallic quasicrystalline alloys of the metal–metal type. The available information bearing on the dynamic and thermodynamic properties of these systems is, however, insufficient by far, while for many quasicrystals it is practically nonexistent altogether.

The present work was aimed at performing a comparative study of the electronic, vibrational, and superconducting characteristics of binary metallic quasicrystals Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ and of their amorphous counterparts, as derived from heat capacity measurements performed over a wide temperature range (1.5–500 K). The phase structure of these compounds prepared in crystallization of the amorphous alloys of the same composition was studied in considerable detail [1–5] and was identified as quasicrystalline.

The Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ alloys are of interest for a number of reasons. The Zr$_{70}$Pd$_{30}$ alloy can reside in three isostoichiometric phase states, namely, amorphous, icosahedral, and crystalline, and Zr$_{80}$Pt$_{20}$, in two phases, amorphous and icosahedral, thus permitting one to study the effect of change in short-range order without varying the concentrations of the components in the course of the transition from amorphous to icosahedral and crystalline state. Moreover, as found out by us earlier [6, 7], these alloys are superconducting, which offers a possibility not only of experimentally determining their electronic characteristics but of estimating the electron–phonon coupling in the quasicrystal.
talline and amorphous states. The absence of complex magnetic effects also simplifies a structural investigation of the effect of short-range order symmetry on the electronic and vibrational properties of these phases.

2. PREPARATION OF SAMPLES AND THEIR CHARACTERISTICS

The icosahedral quasicrystalline systems Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ were prepared by crystallization of amorphous alloys of the same composition obtained by melt quenching on the outer surface of a rotating copper disk [6, 7]. The structure of the samples thus prepared and the effect of annealing on their state were determined by x-ray diffraction (Cu$\text{K}_\alpha$ radiation) with a DRON-2 diffractometer. The phase identification and lattice parameters were derived from the x-ray diffraction patterns. X-ray diffraction patterns obtained for the icosahedral phases exhibit diffraction peaks, which correspond to the icosahedral structure and were indexed by the Bancel scheme [8].

The temperature dependence of the heat capacity was studied over a wide temperature range (1.5–4.5 K). The low-temperature heat capacity of the samples was measured with an adiabatic pulse-heated calorimeter [9]. The experimental error of the heat capacity measurements was 2% in the temperature range 2–4 K, 1% from 4 to 10 K, and 0.2–0.5% within the 10–40-K interval. The superconducting transition temperature was derived from the jump in the heat capacity at midpoint of the superconducting transition.

The high-temperature heat capacity measurements were performed with a differential scanning calorimeter (DSC) permitting high-precision studies of microsamples (10–200 mg) in the temperature range 100–1000 K with an accuracy of ±3%.

3. EXPERIMENTAL RESULTS

The results obtained from measurements of the heat capacity of Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ quasicrystals and their amorphous counterparts are presented in Figs. 1–3 and in the table.

The temperature dependences of the low-temperature (1.5–4.5 K) heat capacities are plotted in Fig. 1 in the $T^2$–$C/T$ coordinates. For comparison, the insets to Fig. 1 depict the resistive transitions of these com-
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The results of the heat capacity measurements in the range 100–500 K are plotted in Fig. 3 in the structural order associated with the transition from the lattice softening with the attendant degradation of the electronic heat capacity measurements of \( T_c \) [6, 7, which supports the volume character of the superconductivity.

It can be seen from Fig. 1 that, in the low-temperature range, the experimental heat capacity data can be well fitted by a relation of the form \( C = \gamma(0)T + \beta T^3 \), which plots as a straight line in the \( C/T \) vs. \( T^2 \) coordinates. Note that, in quasicrystalline \( Zr_{70}Pd_{30} \), this relation persists over a wider temperature interval than it does in the amorphous phase. Within 3–6 K, the rms deviation of experimental data from the \( C = \gamma(0)T + \beta T^3 \) relation is about 1.5%. The least-squares estimates of the \( \gamma(0) \) and \( \beta \) coefficients, as well as the high-temperature limit of the Debye characteristic temperature \( \Theta_{LT} \) related with \( \beta \) through the expression \( \beta = 12\pi^2 R/5 \Theta_{LT}^3 \), are presented in the table. Hereafter, \( R \) is the universal gas constant.

A comparison of the electronic heat capacity coefficients for the icosahedral and amorphous phases suggests a decrease in the density of states on the Fermi surface in the \( Zr_{70}Pd_{30} \) and \( Zr_{80}Pt_{20} \) icosahedral phases as compared to the corresponding amorphous phases.

The results obtained permitted estimation of the characteristic Debye temperatures \( \Theta_{HT} \) and \( \Theta_{LT} \) for these phases in the \( 4.5–40.0 \) K temperature interval, which evidence a substantial decrease in the values of \( \Theta(T) \) and, hence, lattice softening with the attendant degradation of structural order associated with the transition from the icosahedral to amorphous phases.

The results of the heat capacity measurements in the range 100–500 K are plotted in Fig. 3 in the \( (C - 3R)/T \) vs. \( T^3 \) coordinates. The high-temperature parameters, namely, the Debye temperature \( \Theta_{HT} \) and the \( B \) term, were determined graphically from the relation

\[
(C_p - 3R)/T = 3R \Theta_{HT}^2/20T^3 + B,       \tag{1}
\]

where \( C_p \) is the total heat capacity at constant pressure, \( B = (A + \gamma_{HT}) \) is the coefficient of the linear-in-temperature term in the high-temperature range, \( \gamma_{HT} \) is the coefficient of high-temperature electronic heat capacity related with \( \gamma(0) \) through \( \gamma(0) = \gamma_{HT}(1 + \lambda) \), and \( A \) is the anharmonicity parameter. The values of \( \Theta_{HT}, B, A, \) and \( \gamma_{HT} \) for the systems under study are listed in the table.

Examining the table, it becomes evident that the transition from the amorphous to quasicrystalline state brings about a decrease in the coefficients of both the term linear in temperature and of the cubic term, with the corresponding changes for \( Zr_{70}Pd_{30} \) being ~10 and ~30%, and for \( Zr_{80}Pt_{20} \), ~30% and ~40%, respectively.

The change in the superconducting transition parameters suggests that, in the quasicrystalline phases \( T_c \) is lower than that in the amorphous ones. Incidentally, in quasicrystalline phases, \( \gamma(0) \) decreases and the low-temperature Debye parameter \( \Theta_{LT} \) increases. These changes imply a decrease in the density of states in the quasicrystal, and a phonon spectrum rearrangement. For both quasicrystals one observes a decrease in the density of phonon states in the low-frequency range. As regards the high-frequency part of the \( g(\omega) \) function characterized by the \( \Theta_{HT} \) parameter, for quasicrystalline \( Zr_{70}Pd_{30} \), the experiment argues for a hardening of the \( g(\omega) \) spectrum, whereas the spectrum for \( Zr_{80}Pt_{20} \) becomes softer.
Parameters of Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ systems in crystalline and amorphous states

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ZrPd (am)</th>
<th>ZrPd (qc)</th>
<th>ZrPt (am)</th>
<th>ZrPt (qc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$, K</td>
<td>2.6</td>
<td>2.1</td>
<td>3.5</td>
<td>2.48</td>
</tr>
<tr>
<td>$C_{\text{el}}/C_{\text{el}}(T_c)$</td>
<td>1.28</td>
<td>0.17</td>
<td>1.76</td>
<td>0.4</td>
</tr>
<tr>
<td>$\gamma(0)$, mJ/g-at. K$^2$</td>
<td>5.25</td>
<td>4.75</td>
<td>4.15</td>
<td>2.75</td>
</tr>
<tr>
<td>$\beta$, mJ/g-at. K$^4$</td>
<td>0.195</td>
<td>0.114</td>
<td>0.43</td>
<td>0.24</td>
</tr>
<tr>
<td>$\Theta_{LT}$, K</td>
<td>215</td>
<td>260</td>
<td>166</td>
<td>199</td>
</tr>
<tr>
<td>$B$, mJ/g-at. K$^2$</td>
<td>293</td>
<td>315</td>
<td>319</td>
<td>294</td>
</tr>
<tr>
<td>$\gamma_{HT}$, mJ/g-at. K$^2$</td>
<td>3.8</td>
<td>7.5</td>
<td>6.4</td>
<td>9.5</td>
</tr>
<tr>
<td>$A$, mJ/g-at. K$^2$</td>
<td>0.5</td>
<td>4.4</td>
<td>3.95</td>
<td>7.8</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.58</td>
<td>0.54</td>
<td>0.69</td>
<td>0.59</td>
</tr>
<tr>
<td>$N_{\text{Rg}}(0)$, eV states/atom</td>
<td>0.70</td>
<td>0.66</td>
<td>0.52</td>
<td>0.37</td>
</tr>
<tr>
<td>$\Omega$, K</td>
<td>141.05</td>
<td>183</td>
<td>177</td>
<td>177</td>
</tr>
<tr>
<td>$\Omega_{-1}$, K</td>
<td>142.05</td>
<td>160</td>
<td>153</td>
<td>167</td>
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<tr>
<td>$\Omega_{-2}$, K</td>
<td>114</td>
<td>144</td>
<td>100</td>
<td>123</td>
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<tr>
<td>$\Omega_{\log}$, K</td>
<td>179</td>
<td>190</td>
<td>176</td>
<td>190</td>
</tr>
<tr>
<td>$\Omega_{2}$, K</td>
<td>210</td>
<td>225</td>
<td>225</td>
<td>213</td>
</tr>
<tr>
<td>$\Omega_{a}$, K</td>
<td>272</td>
<td>276</td>
<td>284</td>
<td>256</td>
</tr>
<tr>
<td>$\Omega^{\text{HT}}$, K</td>
<td>272</td>
<td>290</td>
<td>290</td>
<td>275</td>
</tr>
</tbody>
</table>

Note: $T_c$ is the superconducting transition temperature; coefficients $\gamma(0)$ and $\beta$ fit the low-temperature heat capacity to the relation $C = \gamma(0)T + \beta T^3$; $\Theta_{LT}$ is the low-temperature Debye characteristic parameter; $\Theta_{HT}$ is the high-temperature Debye characteristic parameter; $B = (A + \gamma_{HT})$ is the coefficient of the linear-in-$T$ term in the high-temperature region; $A$ is the anharmonicity parameter; $N_{\text{Rg}}(0)$ is the density of states on the Fermi surface; $\Omega$, $\Omega_{-1}$, $\Omega_{-2}$, $\Omega_{\log}$, $\Omega_2$, $\Omega_a$, and $\Omega^{\text{HT}}$, characterize, in accordance with Eqs. (6)-(9), the average frequencies (moments) of the vibrational spectrum expressed in units of temperature; $\lambda$ is the electron–phonon interaction constant; $\gamma_{\text{ph}}$ is the electronic heat capacity coefficient in the high-temperature region; and $N_{\text{Rg}}(0)$ is the nonrenormalized density of states.

4. ANALYSIS AND DISCUSSION OF THE RESULTS

The data obtained permitted isolation of the phonon contribution from the experimentally measured heat capacity over a wide temperature range, and determination of the temperature dependence of the characteristic Debye parameter $\Theta$ (Fig. 3), as well as calculation of some average frequencies (moments) of the phonon spectrum.

In separating out the phonon contribution to the heat capacity, we assumed the phonon component of heat capacity $C_{\text{ph}}$ to be related in the harmonic approximation with the heat capacity at constant pressure $C$ measured in experiment through

$$C = C_{\text{ph}} + C_a,$$

where $C_a$ combines the contributions to the heat capacity depending linearly on temperature and originating from anharmonic effects, thermal lattice expansion, and conduction electrons; $\gamma(0)$ is the coefficient of electronic heat capacity of a superconductor in normal state at low temperatures; $B$ is the coefficient of the linear-in-temperature term at high temperature; $R$ is the gas constant; and $n$ is the number of atoms in a formula unit (in our case, $n = 1$).

The interpolation expression (3) for $C_a$ provides the corresponding linear-in-temperature asymptotic relations for both the low- and high-temperature ranges and traces a smooth transition between the low- and high-temperature asymptotics similar to the Nernst–Lindemann law [11]. Note that the contribution of $C_a$ to the total heat capacity within the 20–120-K interval is not over a few percent of the phonon contribution, which justifies the simplicity of the relation (3) employed for description of $C_a$.

The coefficients $\gamma(0)$ and $A$ were found by successive fitting of asymptotic expansions to experimental data in the low- and high-temperature ranges.

At low temperatures, we used the standard expression $C = \gamma(0)T + \beta T^3$, which fits the experimental data within the ~3–6-K interval with an rms deviation of ~1.5%. The values of $\gamma(0)$, $\beta$, and the low-temperature limit of the characteristic Debye temperature $\Theta_{LT}$ related with $\beta$ through $\beta = 12\pi^2 nR/(5 \Theta_{LT}^3)$ are listed in the table.

At high temperatures, the total heat capacity was approximated by the relation with three fitting parameters ($\Omega_2$, $\Omega_a$, and $B$):

$$C = C_{\text{ph}} + C_a = 3\pi R \left\{ 1 - \frac{1}{12} \left( \frac{\Omega_2}{T} \right)^2 + \psi \left( \frac{\Omega_a}{T} \right) \right\} + B \left( \frac{C_{\text{ph}}}{3nR} \right)^2 T,$$

where

$$\psi(z) = \frac{z^2 \exp(z)}{[1 - \exp(z)]^2} \left( 1 - \frac{z^2}{12} \right).$$

To describe the phonon component of the heat capacity, we chose an approach similar to the one employed in [12, 13], more specifically, we used an asymptotic expansion of phonon heat capacity in a
small parameter \( z = \Omega/T \) (where \( \Omega \) is the characteristic phonon energy and \( T \) is the temperature):

\[
C_{\text{ph}} = 3nR \left\{ 1 - \sum_{k=2}^{\infty} \frac{(k-1)B_k}{k!} \left( \frac{\Omega_k}{T} \right)^{k} \right\}.
\]

(6)

Here, \( B_k \) are the Bernoulli numbers, with all \( B_k \) with odd values of \( k > 2 \) being zero.

In Eq. (4), the correction of second order in \( \Omega/T \) is written out separately, and the \( \psi(\Omega_k/T) \) function includes all higher corrections in the Einstein approximation, i.e., assuming \( \Omega_k = \Omega \), for all \( k \geq 4 \).

The quantities \( \Omega_k \) are characteristics of the moments (average frequencies) of the phonon spectrum:

\[
(\Omega_k)^k = \langle \Omega^k \rangle = \int_0^\infty g(\omega) \omega^k f(\omega) \log \left( \frac{T}{\omega} \right) d\omega.
\]

(7)

Here, \( g(\omega) \) is the energy density of phonon states and \( \omega \) is the energy in units of temperature.

Note that, in expansion (4), the term with \( \Omega_\ast \) includes higher order corrections, \( k \geq 4 \), and, therefore, \( \Omega_\ast \) is dominated by the fourth and sixth moments of the phonon spectrum, i.e.,

\[
\Omega_\ast = \Omega_4, \Omega_6.
\]

(8)

The quantities \( \Omega_2, \Omega_4, \) and \( B \) were found by least-squares fitting of the heat capacity to Eq. (4) in the range \( 115–500 \) K. The best fit to experimental data reached by us in this temperature range was with an rms of \( \sim 3\% \). The values of the parameters \( B, \Omega_2, \) and \( \Omega_4 \) are listed in the table. Also presented is the high-temperature Debye temperature limit \( \Theta_{HT} \) related with the second moment of the phonon spectrum through

\[
\Theta_{HT} = \left( 3/5 \right)^{1/2} \Omega_2.
\]

(8a)

Our analysis performed in the harmonic approximation isolated the phonon contribution \( C_{\text{ph}} \) from the total heat capacity by excluding the electronic and anharmonic terms with the use of Eqs. (2) and (3) and provided the values of parameters \( B \) and \( \gamma(0) \) estimated by successive approximations.

Some moments of the phonon spectrum are directly expressed through integrals of the phonon heat capacity [14]:

\[
\Omega = \langle \omega \rangle = \int_0^\infty \left( 1 - \frac{C_{\text{ph}}}{3nR} \right) dT,
\]

\[
\Omega_{-1} = \langle \omega^{-1} \rangle = \frac{3}{\pi} \int_0^\infty C_{\text{ph}} T^{-2} dT.
\]

These moments were found numerically; in the 2–500-K interval, exponential points were used in the integration. Within the temperature range where the interval between the experimental values of the heat capacity was in excess of 10 K, power-law interpolation with a standard confidence interval of \( \leq 5\% \) of the interpolated quantity was employed, while for \( T < 2 \) K and \( T > 500 \) K, the heat capacity was extrapolated following the low-temperature asymptotics of the kind of \( C_{\text{ph}} = \beta T^3 \) and the high-temperature asymptotics in the Debye spectrum model, as was done in [15].

The average frequencies corresponding to these moments are listed in the table, with all the frequencies expressed in units of temperature. The meaning of the quantities \( \Omega_2, \Omega_4, \Omega_6, \) \( \Omega_{\ast} \) is defined by relations (7) and (8), and that of \( \Omega_{\log} \) by the relation

\[
\log(\Omega_{\log}) = \frac{\langle \omega^{-1} \log \omega \rangle}{\langle \omega \rangle} = \int_0^\infty \frac{g(\omega) \log \omega}{\langle \omega \rangle} d\omega.
\]

(9)

Note that the higher order moments \( (\Omega_2, \Omega_4, \) and \( \Omega_{\ast} \) ) reflect the characteristics of the phonon spectrum at higher energies and are determined primarily by the behavior of the heat capacity in the high-temperature range. These values, obtained by approximating the heat capacity by analytical relation (4) in the range \( 115–500 \) K, correlate satisfactorily with the value of \( \Theta_{HT} \) derived from a graph and analytical analysis of the high-temperature heat capacity with the use of Eq. (1). The observed 7\% systematic overestimation of \( \Theta_{HT} \) as compared to the higher-order moments \( (\Omega_2, \Omega_4, \) and \( \Omega_{\ast} \) ) should be assigned to differences between the methods used to expand \( C_p(T) \) in the high-temperature range.

Now, the \( \Omega_{\log}, \Omega_2, \) and \( \Omega_{-1} \) moments characterize the low-energy range and are determined primarily by the low-temperature heat capacity. In the systems under consideration, the \( \Omega_2 \) moment, for instance, is determined by the range of temperatures up to \( 50 \) K and reflects the spectrum at energies from 0 to 25 meV.

The quantities characterizing the low-frequency vibrational range \( (\Omega_{\log}, \Omega_2, \) and \( \Omega_{-1} \) ) in amorphous systems are smaller than those in quasicrystalline ones, so that the low-frequency range of the phonon spectrum
of amorphous systems is “softer.” As for the $\Omega_2$, $\Omega_3$, and $\Omega_H^*$ moments reflecting the higher-frequency spectral range, here, by contrast, it is the spectrum of the Zr$_{80}$Pt$_{20}$ quasicrystalline system that is “softer,” and that of Zr$_{70}$Pd$_{30}$, “harder.”

5. CONCLUSIONS

Thus, our studies have revealed changes in the electronic and phonon spectra and electron–phonon interaction associated with the sample structure. The results obtained allowed us to draw the following conclusions.

(1) Low-temperature measurements have revealed jumps in the heat capacity originating from the transition to superconducting state in the Zr$_{70}$Pd$_{30}$ and Zr$_{80}$Pt$_{20}$ icosahedral quasicrystals and their amorphous counterparts. A comparison of the electronic heat capacity coefficients obtained for the icosahedral and amorphous phases suggests a decrease in the density of states on the Fermi surface in the icosahedral phases. The experimental heat capacity data have yielded estimates of the electron–phonon coupling $\lambda$ and of the density of states $N_{BS}(0)$ in terms of McMillan’s theory. Both quantities, $\lambda$ and $N_{BS}(0)$, increase with decreasing structural order in the low-temperature range. The decrease in the superconducting transition temperature $T_c$ in quasicrystals as compared to their amorphous counterparts should be attributed to a decrease in the density of states on the Fermi surface, a hardening of the phonon spectrum, and weakening of the electron–phonon interaction.

(2) The data obtained on the high- and low-temperature heat capacity have been used to isolate the phonon contribution to the heat capacity, to calculate the main integral characteristics of the vibrational spectra (average phonon frequencies (moments) of the phonon spectrum and the characteristic Debye temperatures $\Theta$), and to compare the vibrational properties of the systems studied. It was shown that changes in the phonon subsystem occur in both the low- and the high-energy parts of the vibrational spectrum. The transition from the amorphous state to the quasicrystalline state in Zr$_{70}$Pd$_{30}$ is accompanied by a hardening of the spectrum at both low and high frequencies. On the other hand, in the Zr$_{80}$Pt$_{20}$ system, the phonon spectrum of quasicrystals is “harder” at low frequencies and “softer” in the high-frequency range as compared to the amorphous counterpart. The anharmonicity of thermal lattice vibrations of both systems is stronger for quasicrystals.

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