

# Dielectric phase transition in the superconducting compounds $\text{HfV}_2$ and $\text{ZrV}_2$ (C15)

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The anomalous behavior of the temperature dependences of the resistivity and magnetic susceptibility indicates that in the compounds  $\text{HfV}_2$  and  $\text{ZrV}_2$  a phase transition takes place with partial dielectrization of the electron spectrum. At temperatures below the transition temperature a nonlinear increase of the conductivity in an electric field is observed.

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The phase transition accompanied by the onset of a dielectric gap in the electron spectrum and of a charge-density wave (CDW) manifests itself most pronouncedly in quasi-one-dimensional metals.<sup>(1,2)</sup> For three-dimensional metallic systems, the dielectrization is as a rule incomplete and the gap in the electron spectrum, according to prevailing notion, occurs only on a certain definite part of the Fermi surface, near which the electron spectrum satisfies the symmetry condition<sup>(2,3)</sup>:

$$\zeta(\mathbf{p}) = -\zeta(\mathbf{p} + \mathbf{Q}) \quad (1)$$

( $\zeta$  is the energy reckoned from the Fermi level and  $\mathbf{Q}$  is some preferred vector). This partial dielectrization can manifest itself in a number of singularities of the electronic properties of the metal below the phase-transition temperature. We present here the results of an investigation of the temperature dependences of the resistivity and of the magnetic susceptibility in the compounds  $\text{HfV}_2$  and  $\text{ZrV}_2$ , as well as of the influence of electric and magnetic fields on the temperature dependence of the resistivity.

The investigated  $\text{HfV}_2$  and  $\text{ZrV}_2$  samples were smelted in an arc furnace in an atmosphere of purified argon and were subsequently heat-treated to ensure that the samples were single-phase. The resultant samples were polycrystals with cubic structure of the C15 type. The resistivity was measured by four-probe dc null method. The magnetic susceptibility was measured by the relative Faraday method with an electronic microbalance with automatic compensation. All the measurements were made in the temperature interval 4.2–300 K. The superconducting transition temperature  $T_c$  was  $8.9 \pm 0.1$  K for the  $\text{ZrV}_2$  samples and  $9.0 \pm 0.1$  K for  $\text{HfV}_2$ .

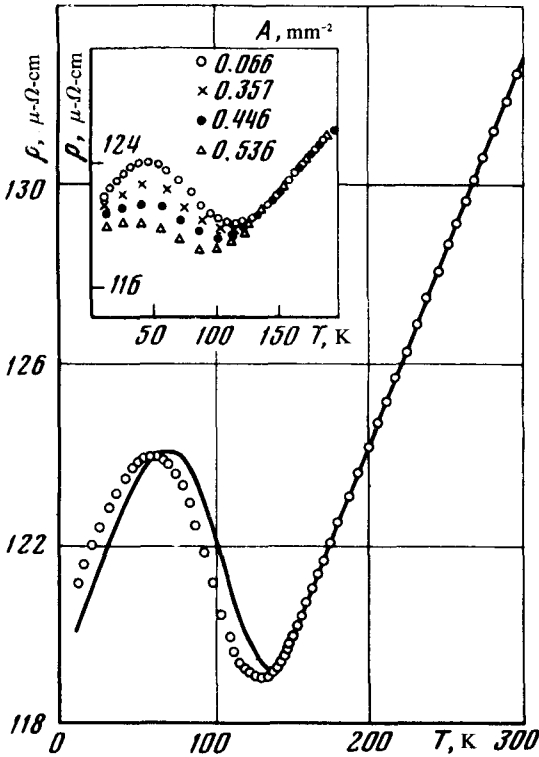


FIG. 1. Temperature dependence of the resistivity  $\rho(T)$  at different values of the field  $E$ ; solid line—theoretical curve in model (2).

Figures 1 and 2 show the results of the measurements of the resistivity  $\rho(T, E)$  for different current densities ( $E$  is the electric field in the sample) and the magnetic susceptibility  $\chi(T)$  in  $\text{HfV}_2$  alloys. Similar plots are obtained also for the  $\text{ZrV}_2$  samples. As seen from the plots in Figs. 1 and 2, at temperatures  $T < T_p = 130$  K there is a clearly pronounced anomalous behavior of the investigated characteristics, as revealed by the presence of a section with negative temperature coefficient of the resistivity and by a change in the temperature dependence of the magnetic susceptibility. When the magnetoresistance was measured in a field  $H = 40$  kOe, the section with the negative temperature coefficient on the plot of  $\rho(T) = \rho(T, E \rightarrow 0)$  shifted towards higher temperatures, and  $T_p$  increased accordingly by  $5^\circ$  (no change in the resistivity in a mag-

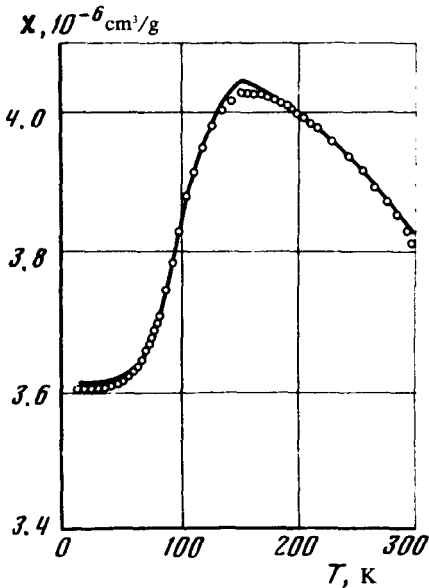


FIG. 2. Temperature dependence of the magnetic susceptibility  $\chi(T)$ ; solid line—theoretical curve in model (2).

netic field was observed at temperatures above  $T_p$  and below  $T' \approx 50$  K, i.e., in the region where the temperature dependence of the resistivity has a metallic character). It should be noted that deviations from stoichiometry of the alloy compositions and introduction of impurities lead to the vanishing of the anomalies on the temperature dependences of  $\rho(T)$  and  $\chi(T)$ .

It is known that a structural phase transition accompanied by lattice distortion takes place in C15 compounds, as in many other transition-metal compounds.<sup>(4)</sup> The experimental results cited above attest, in our opinion, that the number of free carriers in the compounds under consideration change in the course of the structural transition as the result of formation of a dielectric gap on part of the Fermi surface. If it is assumed that the Fermi surface is multiply connected and has closed sections that are similar in shape and for which condition (1) is satisfied, then the expressions for the conductivity  $\sigma(T) = \rho^{-1}(T)$  and the magnetic susceptibility can be written in the form of a sum of additive components

$$\sigma(T) = \sigma_n(T) + \sigma_d(T); \quad \chi(T) = \chi_n(T) + \chi_d(T), \quad (2)$$

where  $\sigma_d(T)$  and  $\chi_d(T)$  describe the contribution of the carriers whose spectrum acquires a gap  $\Delta(T)$  at  $T < T_p$ ,<sup>(5)</sup> while  $\sigma_n$  and  $\chi_n$  describe the contribution of the remaining non-dielectrized part of the carriers. For  $T \ll \Delta(T)$  both  $\chi_d$  and  $\sigma_d$  are proportional to  $\exp[-\Delta(T)/T]$ . The temperature dependence of  $\Delta(T)$  in the simplest case is the same as in the BCS theory.<sup>(3)</sup> It is easily seen that expressions (2) describe qualitatively the experimental  $\rho(T)$  and  $\chi(T)$  plots, while the observed anomalies on these plots are connected with the freezing-out of some of the free carriers. This model explains the dependence of the temperature anomalies of  $\rho(T)$  and  $\chi(T)$  on the compo-

sition and on the introduction of impurities, as well as the change of the resistivity in a magnetic field.<sup>(3)</sup> (We note that the superconducting transition temperature was weakly dependent on the sample composition and on the introduced impurities, so that the dielectrization apparently does not effect the electrons that take part in the superconductivity).

The most interesting result is the clearly pronounced non-Ohmic character of the conductivity in the temperature region  $T < T_p$ . Figure 1 shows the results of measurements of the resistivity at different current densities, i.e., at different values of the electric field  $E$  in the sample. The sample heating following the increase of the current density was apparently negligible, since an increase of the conductivity was observed in the entire temperature interval  $T < T_p$  and was absent at  $T > T_p$ . The value of  $T_p$

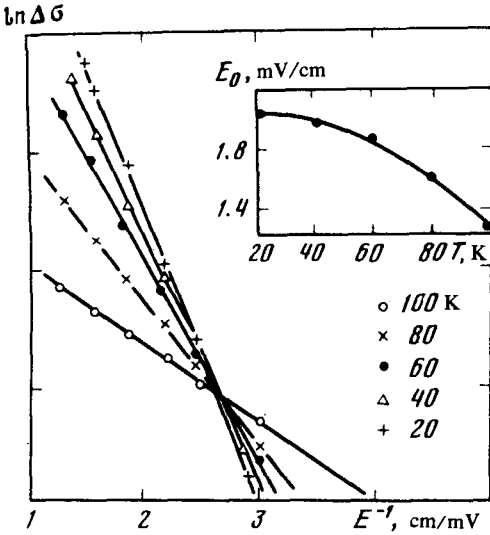


FIG. 3. Plot of  $\Delta\sigma(T, E)$  against  $1/E$  for different temperatures, temperature dependence of the "activation field"  $E_0(T)$ .

was independent of  $E$ . Figure 3 shows in a semi-log scale plots of  $\Delta\sigma(T, E) = \sigma(T, E) - \sigma(T, E \rightarrow 0)$  against the fields for various temperatures. As seen from Fig. 3,  $\Delta\sigma(T, E)$  is well described by the law

$$\Delta\sigma(T, E) = a(T) \exp[-E_0(T)/E]. \quad (3)$$

The same figure shows the temperature dependence of the "activation field"  $E_0(T)$ . A similar nonlinear character of the conductivity was recently observed in the quasi-one-dimensional metal TTF-TCNQ<sup>(6)</sup> and in the compound NbSe<sub>3</sub><sup>(7)</sup> below the metal-insulator transition temperature. (In NbSe<sub>3</sub>, just as in our case, the dielectrization is incomplete and affects only a certain part of the Fermi surface.) The causes of this anomalous character of the conductivity are not fully clear. It is quite probable, however, that such an increase of the conductivity in a field is a characteristic property of systems in which dielectrization of the electron spectrum takes place as a result of the dynamics of the charge-density wave produced in the dielectric phase transition.<sup>(6-8)</sup> It is interesting that the mechanism considered in<sup>(8)</sup> and contributing to the conductivity on account of the CDW is described precisely by expression (3).

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<sup>3</sup>Yu.V. Kopaev, *Tr. Fiz. Inst. Akad. Nauk SSSR* **86**, 3 (1975).

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<sup>8</sup>K. Maki, *Phys. Rev. Lett.* **39**, 46 (1977).