

Local distortions, insulating regions, and nature of the high-resistance state in titanium- and zirconium-based metastable alloys

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A quantum size effect is hypothesized in the electron spectrum in disperse particles of an ω phase, on the basis of an analysis of features of the structural state of the lattice of metastable titanium and zirconium alloys and the electronic structure of the ω phase. Analysis of the scattering of "external" electrons by such regions leads to an understanding of the basic reasons for the formation of the high-resistance state in these alloys. Resistive anomalies and structural anomalies (local distortions) in dilute alloys are explained under the assumption that small quasicrystalline (icosahedral) clusters form.

Among various metallic systems there is special group of high-resistance alloys which have a high residual resistance ρ_0 ($\rho_0 \sim 10^2 - 10^3 \mu\Omega \cdot \text{cm}$) and a negative temperature coefficient of the resistance, $d\rho/dT < 0$ (Ref. 1). Many of these alloys have a "pseudogap" in their electron spectrum near the Fermi level E_F (Refs. 2–6), which can be seen clearly in, for example, optical spectra.^{2–4} The temperature dependence and the magnetic-field dependence of the resistance in several of these alloys are so unusual that investigators striving for a qualitative understanding of these alloys have invoked the extremely exotic proposition that localized and itinerant states could coexist at E_F (Refs. 5 and 6). One then runs into a fundamental problem: Why does a discrete level not spread out and enter a continuum? (This is a problem of the suppression of hybridization.) In the present letter we propose a physical picture which, in contrast with earlier suggestions, leads to a qualitative solution of this problem. It also explains known correlations of resistive anomalies with features of the structural state of these alloys.^{3,4,7,8}

We conduct the discussion using as an example titanium and zirconium alloys, which are the groups of high-resistance alloys that have been studied most thoroughly.

The main conclusion about titanium and zirconium high-resistance alloys is that they are polyphase metastable systems, and that their electronic properties depend strongly on not only the concentrations of the components, but also the temperature and quenching conditions. These properties are directly related to the phase composition of these alloys.^{7,9,10} Although this circumstance is obvious to metallurgists, it has been ignored in all previous theoretical analyses of these alloys. It forms the basis of

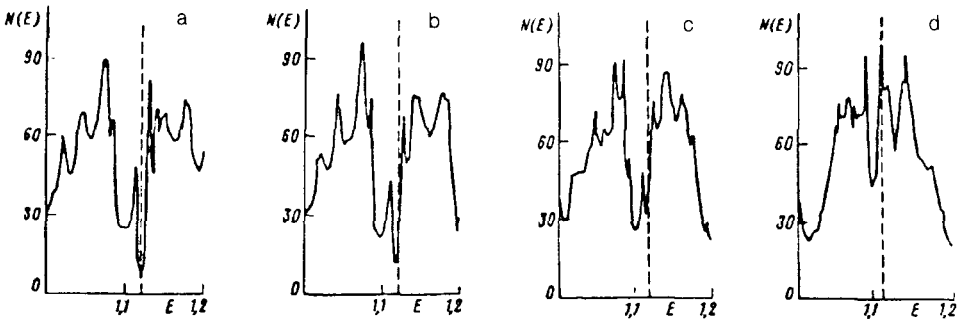


FIG. 1. Density of electron states $N(E)$ per cell (of three atoms) in the ω phase of Ti. a—Ideal ω phase (the displacement of the planes is $u = u_0$); b— $u = 0.8u_0$; c— $u = 0.6u_0$; d— $u = 0.4u_0$. The energy E is in rydbergs, and the density of states is in reciprocal rydbergs. The dashed line is E_F .

our discussion. Specifically, we work from the two following premises.

1. The metastable binary alloys $Ti_{1-x}Me_x$ and $Zr_{1-x}Me_x$, where Me is a $3d$ or $4d$ metal to the right of Ti (or Zr) in the periodic table, have an hcp structure with local distortions (α') at $x < x_c$ and a $\beta + \omega$ structure at $x > x_c$, where β is a bcc structure, and ω is a phase obtained from β through a tripling of the period along the $\langle 111 \rangle$ direction. This phase exists in the form of small ($\sim 20\text{--}60 \text{ \AA}$) intrusions of an equiaxial or ellipsoidal shape which are ordered in a "superlattice." With increasing x , the size of these intrusions decreases, and the ω phase deviates more and more from perfection (i.e., the displacement of the lattice planes along $\langle 111 \rangle$ occurs at the intermediate point between the ideal ω phase and the β phase). The high-resistance alloy corresponds to the $\beta + \omega$ region. The resistance maximum corresponds to the composition with the maximum of diffusion scattering.^{3,4} The total volume of the ω phase is^{7,9} about 30–40%. A disperse nature of the ω phase and an ordering of its precipitates in a superstructure constitute the first premise of this approach.

2. The second premise is a specific electronic structure of the ω phase, as shown in Fig. 1 (calculation results were graciously furnished by A. I. Lichtenstein of the Max Planck Institute in Stuttgart). A characteristic feature of the density of electronic states $N(E)$ of the ideal ω phase ($u = u_0$) and the nonideal ω phase ($u/u_0 > 0.7$) is the presence of a narrow, deep dip in the immediate vicinity of E_F . We assume that $N(E)$ retains qualitatively the same shape in the alloy on the basis of considerations regarding its favorability from the energy standpoint.¹¹ As a starting point we assume that the $\beta - \omega$ interface is completely impenetrable to conduction electrons. The electron spectrum in the ω phase must then be quantized. The characteristic distance between levels is

$$\Delta \approx \frac{1}{N(E)} \frac{\Omega_0}{\Omega} \quad (1)$$

and is particularly large near E_F . Here Ω is the volume of the ω region, and Ω_0 is the volume of a unit cell. Working on the basis of the results of calculations on $N(E)$ and

data on the dimensions of the ω inclusions, $N(E_F) \simeq (0.1E_F)^{-1}$ and $\Omega/\Omega_0 \simeq 30$, we find the estimate $\Delta \sim 3 \times 10^2$ K near E_F . This figure is 1/100 of the value of E away from the $N(E)$ dip (with a width $\sim 10^{-3}$ Ry). If the β - ω interface is assumed to have a finite penetrability, then we find quantum-size levels of finite width:

$$\Gamma \simeq \pi |V|^2 N(E_F), \quad (2)$$

where V is a matrix element representing the hybridization of the "internal" and "external" electrons. Adopting the natural estimate $V \sim 0.1E_F$, we conclude that the small value of $N(E_F)$ leads to values $\Gamma \ll E_F$, so the estimate $\Gamma \sim 10^2$ K $\sim \Delta$ seems to be justified. There is, however, a mechanism which is capable of substantially reducing the value of Γ . As was shown in Ref. 12, if the distance from the quasilocal level to E_F and its width Γ are smaller than the characteristic phonon frequency $\bar{\omega}$, then for the typical values of the electron-phonon coupling constant, $\lambda \sim 0.1-0.5$, the value of Γ can decrease by an order of magnitude or more, because of a "polaron narrowing" of the level. Taking this circumstance into account, we conclude that the condition $\Gamma \ll \Delta$ apparently holds and that the spectrum of particles of the ω phase is discrete. These results are evidence that these particles are in an insulating state.

As a result, when the external electrons are scattered from these regions, a resonance corresponds to each discrete level (the scattering phase shift is $\delta \sim \pi/2$). The situation is reminiscent of that which arises in the scattering of neutrons by nuclei. This circumstance can apparently explain the sharp increase in the resistance observed upon the appearance of these ω -phase regions. Noting that the particles of the ω phase are ordered in a superlattice, we see the reason for the observed appearance of a pseudogap in the spectrum: The latter is always observed for electrons in a lattice of resonant scatterers.¹¹ Finally, a coexistence of localized electron states (in the insulating regions) and itinerant ones (in the β -phase region) near E_F , as postulated in Refs. 5 and 6 in order to explain the temperature dependence and the magnetic-field dependence of the electrical resistance, fits in a natural way into this picture.

The entire discussion above referred to all metastable alloys based on Ti and Zr with an α -(β + ω) transition. We now note that there are fundamental distinctions between $\text{Ti}_{1-x}\text{V}_x$ alloys, with their unbounded solubility in the high-temperature β phase, and the alloys which have a low impurity solubility in both the α and β -phases (the Ti-Fe system is the member of this group which has been studied in most detail). One of the clearest features of the latter system is apparently an independence of the structure of the local surroundings of Fe impurities from the structure of the long-range order (the α' or β' phase), observed in Ref. 8 by means of the Mössbauer effect. According to Ref. 8, when the equilibrium-solubility limit in the α phase, $x^* \sim 10^{-4}-10^{-3}$, is crossed, some surprisingly stable clusters containing iron form. Their structure remains essentially constant up to Fe concentrations $x \simeq 0.2$. The formation of these clusters was explained in Ref. 10 on the basis of the substantial (nearly twofold) difference between the ionic radii of Ti and Fe. Because of this difference, the equilibrium distances between Ti and Fe, corresponding to the minimum of the total energy, are much smaller than the Ti-Ti distance (evidence for this conclusion comes, in particular, from the pronounced "compression" of the intermetallic alloy TiFe, with the CsCl structure, in comparison with β -Ti). As a result, the

metastable alloy $Ti_{1-x}Fe_x$ can be classified as a "frustrated" system in the sense that considerations of energy favorability for small groups of atoms contradict the fact that a long-range order exists. With regard to the specific structure of these clusters, we note the pronounced qualitative similarity between the Mössbauer spectra of $Ti_{1-x}Fe_x$ alloys and icosahedral quasicrystals containing impurity Fe atoms.¹³ At the same time, it is known¹⁴ that there exists an icosahedral Ti_2Fe phase. In this connection, it might be suggested that the local regions observed in Ref. 8 are icosahedral clusters with a composition close to Ti_2Fe and that it is the formation of these clusters at the temperature of quenching from the melt or the β solid solution which determines the distance between the equilibrium α phase and the metastable α' phase (the equilibrium solubility limit $x=x^*$). Such clusters can apparently play an important role in several regards. First, they set the stage for the existence of two-level systems, which are, according to Ref. 15, responsible for the low-temperature minimum ($T \approx 15-20$ K) in ρ in the α' phase (there is no such minimum in $Ti_{1-x}V_x$). Second, being "compressed," they cause a "crystal-chemistry" compression of the matrix, giving rise to an ω phase at values of x much smaller than in $Ti_{1-x}V_x$ (Ref. 7). It is interesting to note that the experimental value of the compression in $Ti_{1-x}Fe_x$ alloys in comparison with pure Ti (as estimated from the data of Ref. 16 on the change in volume and bulk modulus in these alloys) at the point of the $\alpha-(\beta+\omega)$ structural phase transition is approximately equal to the compression of pure Ti at the known pressure for the $\alpha-\omega$ transition, ≈ 60 kbar.

In the physical picture proposed here for titanium and zirconium alloys, we find a natural explanation for the existence of an "electronic" phase transition, which is a diffuse transition along the concentration scale, with an $\alpha-(\beta+\omega)$ structural transition¹⁶ (for $Ti_{1-x}Fe_x$ we have $x_{c1} \approx 0.05$ and $x_{c2} \approx 0.07$). The second critical concentration, x_{c2} , corresponds to a transition from relatively large inclusions of the ideal ω phase to disperse inclusions of a "nonideal" ω phase, which form a superstructure. A detailed explanation of the anomalies in the observed properties at $x=x_{c2}$ (including anomalies in microwave absorption¹⁷) will be the subject of a separate paper.

We note in conclusion that it would be interesting to study the electronic properties of the $Zr_{1-x}Ti_x$ system in the region in which the ω phase exists.¹⁰ If a high-resistance state were to be observed in this system, this observation would be direct evidence that a governing role is played by features of the structural state, not by the fact that there is a difference between the electronic structure of the impurity and the matrix, which has been singled out previously.⁵

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