

Electronic phase transition and anomalies of the lattice properties of disordered titanium alloys

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A new electronic phase transition has been discovered in disordered titanium-based alloys of transition metals. Sharp anomalies in the bulk modulus, in the ultrasonic attenuation factor, and in the electrical conductivity associated with this transition are demonstrated in the particular cases of the Ti-Fe and Ti-Cr systems. The nature of the electronic transition and the mechanism for the structural conversion in titanium alloys are discussed.

Alloys of titanium with transition metals of groups V–VIII, which are quenched from the high-temperature β solid solution or from a melt, exhibit well-known sharp anomalies in their electronic properties (in particular, the residual resistivity ρ_0 increases sharply, and the sign of the thermal factor of the resistivity, $\alpha = d\rho/dT$, goes negative) near a critical density x_c (Ref. 1, for example). These anomalies may indicate important structural changes in the electron energy spectrum near the Fermi level of the alloys. In this concentration region, however, the $\alpha \rightarrow (\beta + \omega)$ structural transition occurs.² It has previously been assumed that there exists a unique x_c at which the structural transition occurs and at which the anomalies are observed in the electronic properties. In this connection, it has frequently been suggested that the reason for the electronic anomalies might be a lattice instability which is most pronounced at the point of the structural transition.

The results which we are reporting here show that actually two phase transitions—a structural transition and an electronic transition—occur, at different concentrations, in these alloys. The anomalies in the electronic properties appear at the second transition.

It is essentially impossible to determine detailed correlations in the concentration behavior of the various physical properties which have been studied by different investigators, because of the serious uncertainties in the reported values of the absolute concentrations of the alloys. Furthermore, the value of the critical concentration may itself vary significantly with the method by which the samples are prepared.² In this letter we are reporting experimental results for samples cut from the same alloy ingots. The ingots are produced in an arc furnace on a water-cooled copper hearth. This procedure resulted in a rate $\sim 10^4$ deg/s of the cooling from the melt. A homogeneous distribution of components was achieved by turning the ingots over and remelting them six times. The samples were subjected to no further heat treatment. The concentrations of the alloys reported here are based on the composition of the initial material

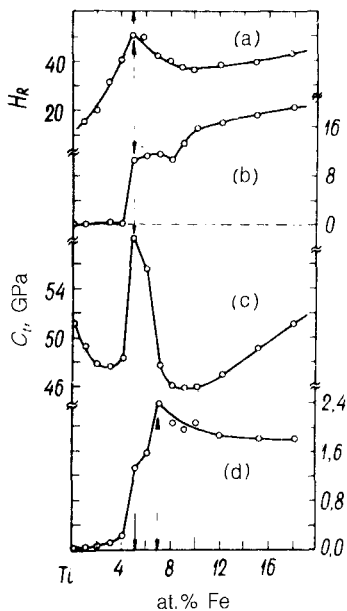


FIG. 1. Concentration dependence of various properties of $Ti_{1-x}Fe_x$ alloys. a—Rockwell hardness; b—deviation of the atomic volume from the “average crystal”; c—shear modulus; d—residual resistivity.

after a monitoring of the ingots by weight. These results have been confirmed by spectral analysis. All the data reported refer to $T = 300$ K.

Figure 1 shows the concentration dependence of the Rockwell hardness H_R (a); the deviation of the atomic volume Ω from the “average-crystal approximation,” i.e., $\Delta\Omega/\bar{\Omega} = (\Omega - \bar{\Omega})/\bar{\Omega} [\bar{\Omega} = x \cdot \Omega_{Fe} + (1-x)\Omega_{Ti}]$, according to calculations from density measurements (b); the shear modulus $C_i = \rho_m v_i^2$ (v_i is the transverse sound velocity) (c); and the residual resistivity ρ_0 (d) in $Ti_{1-x}Fe_x$ alloys. The $H_R(x)$ dependence agrees well with data in the literature.² The maximum on the $H_R(x)$ curve corresponds to the critical concentration for a transition to a bcc structure; in our case, it occurs at 5 at.% Fe. At the same concentration we observe a jump in the atomic volume (on the order of 1%) and a sharp maximum in $C_i(x)$. The maximum of $\rho_0(x)$, however (the critical concentration in terms of electronic properties) occurs at 7 at.% Fe. Near this concentration we also see a deviation of $\Delta\Omega/\bar{\Omega}(x)$ from a monotonic behavior. This result may be evidence of the existence of two critical concentrations, $x_{c1} = 0.05$ and $x_{c2} = 0.07$.

The change to a negative sign of α also occurs at x_{c2} (Fig. 2a). The bulk modulus, $B = \rho_m (v_e^2 - 4/3v_t^2)$ (v_e is the longitudinal sound velocity), exhibits a more complex behavior. The curve of $B(x)$ in Fig. 2b has two sharp maxima against the background of a rather significant ($\sim 7\%$) overall softening of $B(x)$ in the interval $0 < x < 0.12$, as shown by the dashed line. These two sharp maxima occur at x_{c1} and x_{c2} . Finally, the most sensitive indicator of a phase transition—the ultrasonic attenuation coefficient $\Gamma(x)$ —has two sharp maxima at 5 and 7 at.% Fe, as shown in Fig. 2c (the measurements of C_i , B , and Γ were carried out at a frequency of 10 MHz).

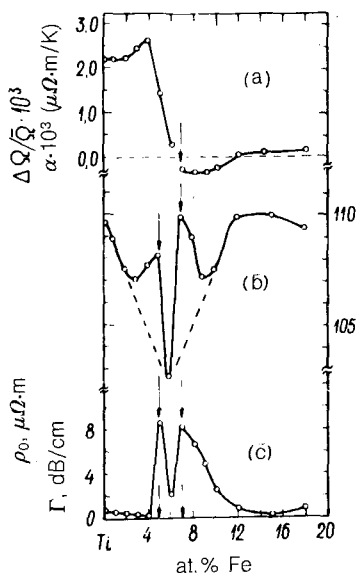


FIG. 2. Concentration dependence of various properties of $Ti_{1-x}Fe_x$ alloys. a—Thermal factor of the resistance; b—bulk modulus; c—ultrasonic attenuation factor.

These results thus show that as the impurity concentration in the titanium alloys is increased, two phase transitions occur. The first, at x_{c1} , is due to a transition hcp (Ti) \rightarrow bcc; the second, at x_{c2} , which occurs on the basis of the bcc structure, is an electronic transition. The absence of an anomaly in $C_t(x)$ at x_{c2} indicates that this second transition does not involve structural changes. We wish to stress that, in contrast with an electronic phase transition of order³ 2.5, the electronic transition seen in the present experiments typically is accompanied by a pronounced anomaly in $B(x)$.

It was shown in Ref. 4 that a key feature of the electronic structure of these alloys is the autonomy of the d -electron subsystem of the impurities with respect to the conduction band of the matrix. As the concentration is increased, a Mott-Hubbard transition occurs in the impurities subsystem, and this transition ultimately is responsible for the appearance of the anomalies in the electronic properties.^{5,6} According to Ref. 6, this transition should be accompanied by anomalies in the lattice properties also. As was shown in Refs. 5 and 6, in materials with autonomous electronic subsystems the Coulomb interaction between these subsystems is of fundamental importance. The exchange-correlation contribution to the Ω potential is singular. It is described by the following expression in the lowest order in the interaction:

$$\Omega_s = \sum_{\mathbf{p}\mathbf{p}'} \int \frac{d\epsilon}{2\pi i} \frac{d\epsilon'}{2\pi i} G(\mathbf{p}\epsilon)G(\mathbf{p}'\epsilon') \left[\frac{4\pi e^2}{(\mathbf{p} - \mathbf{p}')^2 + \lambda^2} \right]^2 (\mathbf{p} - \mathbf{p}')^2 \alpha(\epsilon - \epsilon'), \quad (1)$$

where λ is the reciprocal of the screening length, e is the charge of an electron, $G(\mathbf{p}\epsilon)$ is the Green's function of the conduction electrons, and $\alpha(\omega)$ is the polarizability of the Mott-Hubbard subsystem.⁷ A calculation from (1) in the case in which the system is close to the Mott-Hubbard transition yields the result

$$\Omega_s = 2\beta^2 \ln(1 + 1/\beta) W_d \ln(E_F/\Delta) \quad (2)$$

($\Delta \ll W_d, E_F$) where Δ is the distance between Hubbard subbands, E_F is the Fermi energy, $\beta = (me^2/\pi p_F) \ll 1$, p_F is the Fermi momentum, $W_d = p_F^2 \sum_{\mathbf{k}} [\partial b_{\vec{k}}(\mathbf{k})/\partial k_x]^2 \delta[b_{\vec{k}}(\mathbf{k})]$ is an energy on the order of the width of the impurity band, $b_{\vec{k}}(\mathbf{k}) = t(\mathbf{k} + \vec{k}) - t(\mathbf{k})$, $t(\mathbf{k})$ is the single-electron energy in the d -band, and \vec{k} is the quasimomentum of the exciton condensate.^{5,7} Although expressions (1) and (2) hold under the condition $\beta \lesssim (\Delta/W_d)^2$, incorporating the following orders in β does not change the singular nature of the corresponding contributions.

As the Mott-Hubbard transition is approached ($\Delta \rightarrow 0$), the contribution of (2) to the Ω potential increases, so that proximity to the Mott-Hubbard transition is not preferred from the energy standpoint in a model with states of two types.⁴⁻⁶ The most natural way to get away from the Mott-Hubbard transition and to lower the energy in (2) [through a decrease in $t(\mathbf{k})$ and an increase in Δ] is to switch to a structure with a lower coordination number (from an hcp structure with a $z = 12$ to a bcc structure with $z = 8$). As the concentration is increased further, a Mott-Hubbard transition nevertheless occurs, so that the electronic transition observed at x_{c2} would naturally be identified with a Mott-Hubbard transition in the impurity d -electron subsystem. This transition should be accompanied by anomalies in the elastic moduli, $\delta C_{ik} \sim \partial^2 \Omega_s / \partial u_i \partial u_k \sim \Delta^{-2}$ (u_i are the corresponding components of the strain tensor), which are most pronounced in B , since Δ changes to the greatest extent in the case of a deformation which changes the volume. Analysis of the experimental data leads to the conclu-

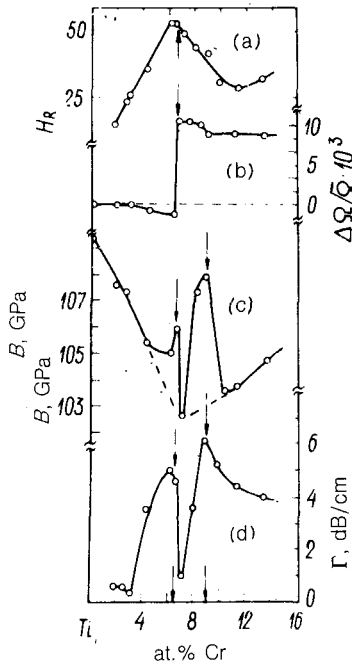


FIG. 3. Concentration dependence of various properties of $\text{Ti}_{1-x}\text{Cr}_x$ alloys. a—Rockwell hardness; b—deviation of the atomic volume from the "average crystal"; c—bulk modulus; d—ultrasonic attenuation factor.

sion that the structural transition occurs because the system reacts to the approach to an electronic transition.

We wish to stress that these conclusions are universal for titanium alloys, as can be seen from the results of a study of these properties in the $Ti_{1-x}Cr_x$ system (Fig. 3; $x_{c1} = 0.064$, $x_{c2} = 0.09$). Ti-Co alloys show a similar behavior (the results will be published separately). The sequence of structural and electronic transitions which we have established here appears to be more general in nature.

In summary, a phase transition of a purely electronic nature has been discovered in titanium-based alloys of transition metals. This transition, which occurs shortly after a structural transformation, is accompanied by anomalies in lattice and electronic properties. The existence of two transitions, at distinct concentrations, can be explained in a simple way by a model with independent electronic subsystems.⁴⁻⁶

The thermal-emf method^{8,9} and the muon method for measuring the Knight shift¹⁰ have proved effective for studying topological electronic transitions in alloys of simple metals. In the alloys which we have been discussing here, the electronic transition is of a different nature, involving far greater changes in the density of electron states near the Fermi level.^{1,4,5} We should therefore expect that the anomalies in the thermal emf and the Knight shift would be more significant here. Furthermore, zirconium-based alloys of transition metals are known to exhibit anomalies in structural state which are the same as for titanium alloys. It would be interesting to determine whether an electronic phase transition occurs in zirconium alloys.

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