Effect of peaks in the electron-state density on structural and magnetic instabilities of alloys

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Narrow peaks in the density of electron states, $N(E)$, near the Fermi level E_F are shown to be an indication of a structural or magnetic instability even if the narrow peaks are separated from E_F by a distance greater than the thermal spread. An explanation is offered for the effect of transition-metal impurities in NiTi on the temperature of the martensitic transition. Ferromagnetism apparently appears in the alloy $Pd_{1-x}Fe_x$ because of the appearance of narrow peaks near E_F. Explicit expressions for $\partial N(E)/\partial x$ incorporating the change in the states of the matrix electrons are proposed.

Identifying the factors that influence the structural and magnetic stability of metals and alloys is of much theoretical and practical importance.[1-4] Calculations of the total energy,[2] despite their complexity, are insufficient since the "competing" phases usually have approximately equal total energies, and the lattice instability is more probably of dynamic origin.[5-7] It is thus customary to use a simpler analysis based on a calculation of[3] $N(E_F)$. This approach was used as early as the 1930s to analyze a structural instability (the Hume-Rothery rules[1]) and a magnetic instability (the Stoner condition[4]), but it has yet to receive a firm footing. At any rate, in the usual single-particle approach one considers only those structural features in $N(E)$ which lie within the thermal spread in E_F ($\lesssim 10^{-2}$ eV). When many-electron effects are taken into account, the situation changes because of a contribution of virtual electronic transitions.[8-10] The prescence of narrow peaks near E_F (at distances on the order of a few tens of electron volts) can lower the stability of a crystal structure because of a softening of the elastic moduli[8] and of the phonon spectra.[9] These peaks can also promote the tendency toward ferromagnetism by virtue of an increase in the Stoner exchange parameter.[8,10] In the present letter we show for the first time in the example of some specific systems (alloys based on NiTi and Pd) that studying the structural features in $N(E)$ near E_F is an effective method for analyzing structural and magnetic instabilities of alloys, in particular, for predicting the effect of impurities on the temperature of the martensitic transition.

The ordered alloy NiTi exhibits a martensitic transition and a "shape memory."[11] Various impurities have important effects on the temperature of the martensitic transition: An excess of Ni sharply reduces this temperature; substitution of F_E for Ni also reduces it, but to a lesser extent; and the substitution of Cu causes a slight increase in this temperature.[11,12] Palladium is the most striking example of a "nearly ferromagnetic" metal.[4] Self-consistent band calculations have been carried out for ordered alloys and isolated impurities by a Green's-function method in the approximation of atomic

spheres[13] through the use of a local spin-density functional.[14] One can derive an explicit expression for $N(E)$ at low impurity concentrations x in the approximation of a coherent potential,[15] in first order in x (by using the methods of Ref. 16 one can show that this formula is formally exact at small values of x). We have

$$N(x, E) = (1-x)N_0(E) + xN_1(E) + x\Delta N(E) \equiv N_0(E) + x\delta N(E), \quad (1)$$

where $N_0(E) = -\pi^{-1}\,\mathrm{Im\,Tr}\,\dot{p}_0(E)T^{00}(E)$ is the state density of the pure crystal, and $T^{00}(E)$ is the complete scattering matrix.[16] In (1), the quantity

$$N_1(E) = -\frac{1}{\pi}\,\mathrm{Im\,Tr}\{\dot{p}_1(E)T^{00}(E)[\,1 + (p_1(E) - p_0(E))T^{00}(E)\,]^{-1}\}$$

is the partial state density of the impurity atom, and $\dot{p}_0(E)$, $\dot{p}_1(E)$ are derivatives of the potential function with respect to the energy. Here

$$\Delta N(E) = \frac{1}{\pi}\,\mathrm{Im\,Tr}\{[1 + (p_1 - p_0)T^{00}]^{-1}(p_1 - p_0)(\dot{T}^{00} - T^{00}\dot{p}_0 T^{00})\}$$

describes the change in the state of the matrix caused by the impurity.

In first order in x, there is no shift in E_F, since the change in the number of electrons as a result of doping, $x\delta Z$, is precisely equal to the number of additional

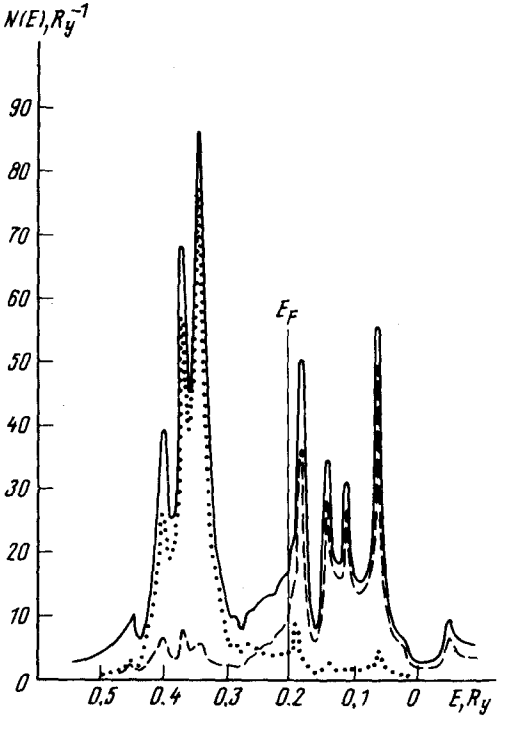

FIG. 1. Density of electron states, $N(E)$ of the intermetallic alloy NiTi in the high-temperature phase (with the CsCl structure). Solid line—total contribution; dashed line—partial contribution of Ti; dotted line—partial contribution of Ni.

states under E_F, by virtue of electrical neutrality. From (1) we find

$$\delta Z = \frac{\partial}{\partial x}\int_{-\infty}^{E_F} dE\, N(x,E) = -\frac{1}{\pi}\,\mathrm{Im\ Tr\ ln}\,\{1+[p_1(E_F)-p_0(E_F)]\,T^{00}(E_F)\} + \frac{\partial E_F}{\partial x}\,N_0(E_F), \tag{2}$$

which we can then use with Lloyd's formula[15] to find $\partial E_F/\partial x = 0$. It follows that the well-known rigid-band approximation must be understood not as a shift in E_F but as a shift of the energy bands with respect to E_F, by an amount $-x\delta Z/N(E_F)$. This situation corresponds formally to a first-order perturbation theory in δZ, i.e., a weak scattering. For transition-metal alloys, it is far more typical to see the appearance of rather narrow quasilocal levels, especially if the impurity d resonances fall in the $N_0(E)$ gap. It can be seen from the calculated results in Fig. 1 that for the intermetallic compound NiTi there is typically a narrow peak 0.25 eV above E_F. This peak is formed primarily by d states of Ti. It is the virtual transitions to the narrow peak that cause the softening of the phonon spectra,[9] which are in turn responsible for the martensitic transition.[5] We thus have an explanation for the experimental facts listed above regarding the effect of substitutional impurities on the stability of the high-temperature phase. It can be seen from Fig. 2 that an excess of Ni leads to a sharp

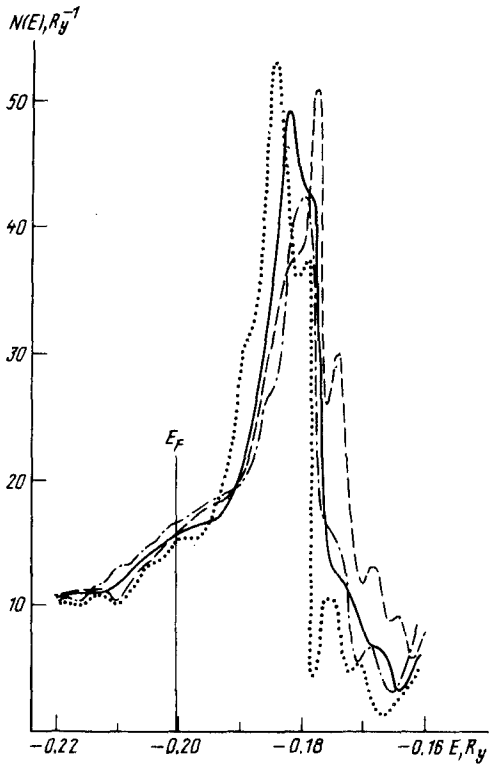

FIG. 2. Results calculated on $N(E)$ for the following alloys: Solid line—NiTi; dashed line—$Ni_{52}Ti_{48}$; dot-dashed line—$Ni_{95}Fe_5Ti_{100}$; dotted line—$Ni_{90}Cu_{10}Ti_{100}$.

disruption of the narrow peak, i.e., increases the stability of the given structure. Doping with Fe also disrupts the narrow peak, but to a lesser extent, while doping with Cu moves the peak slightly toward E_F. The effect should be to accelerate the softening of the phonon spectra.[9] An important role is played by the effect of the impurity on the state of the matrix, which is described by the last term in (1), especially for a Cu impurity. It is clearly inadequate to analyze $N_1(E)$ alone, although calculations are ordinarily limited to such an analysis. The Ni and Fe impurities raise $N(E_F)$ in NiTi (Fig. 2), but without destabilizing the high-temperature phase.[11,12] In other words, the change in $N(E_F)$ is not a governing factor. These calculations thus clearly demonstrate the important role played by specifically virtual electronic transitions in the structural stability of alloys (the "action of narrow peaks at a distance"[8-10]). We might also note that, as can be seen from Figs. 1 and 2, the rigid-band approximation when applied to alloys containing an excess of Ni predicts the incorrect sign of the shift of E_F with respect to the narrow peak. The effect of deviations from stoichiometry on the martensitic transition in NiTi has been studied previously.[17] However, these results of band calculations do not seem reliable, for example, because of the use of a nonstandard averaging procedure, which leads to nonphysical results (a sharpening of the peaks upon an increase in disorder).

The effect of impurities on the magnetic stability has been analyzed for the Fe and Ni impurities in Pd. It is known from experiments that Pd becomes ferromagnetic upon doping with 2.8 at.% Ni or with only 0.1 at.% Fe (Ref. 18). It was suggested in Refs. 8 and 10 that the appearance of a ferromagnetism is a consequence of an increase in the Stoner exchange parameter caused by virtual transitions to quasilocal impurity levels (which give rise to narrow peaks). Since there is a nearly filled narrow peak in pure Pd, this increase should be particularly pronounced if the narrow peaks that arise

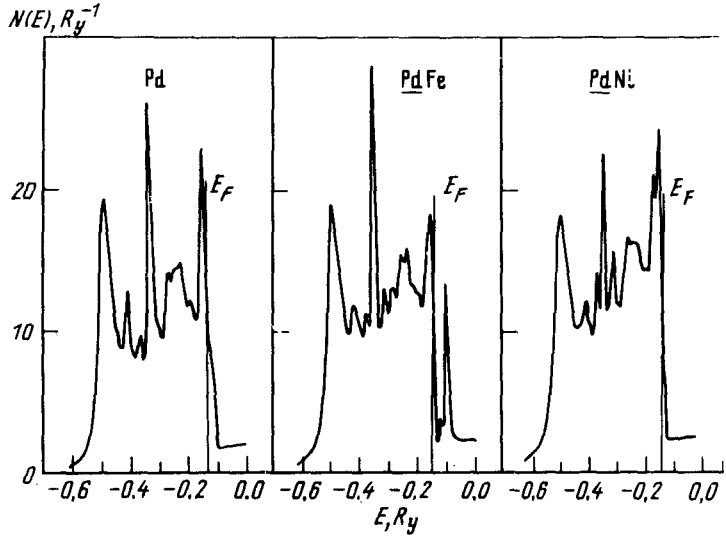

FIG. 3. Total $N(E)$ for Pd, $Pd_{95}Fe_5$, and $Pd_{95}Ni_5$.

are above E_F (an amplification of structural features in the "two-peak" case[8,10]). The results of our calculations (Fig. 3) indicate the appearance of a narrow peak above E_F for the Fe impurity and below E_F for the Ni, explaining the observed picture.[18] As in NiTi, in alloys of Pd there are important effects of a change in the state of the matrix, which significantly intensify the narrow peak for Fe in comparison with that for $N_1(E)$. Finally, we wish to emphasize that Fig. 3 shows that the addition of Fe leads to a decrease in $N(E_F)$; i.e., the "action of the narrow peaks at a distance" seems to also play a governing role in an analysis of the magnetic instability of alloys. We know quite well (in connection with invars, for example) that a change in the magnetic state of an alloy may be accompanied by very sharp anomalies in its elastic and thermodynamic properties. These changes may result from the presence of narrow peaks, whose positions and widths are determined by the size of the magnetic moment and by the type of magnetic order.[19]

In summary, by studying the evolution of $N(E)$ as changes are made in external parameters (the pressure, the concentration, etc.) one can predict the change in the anomalies in the electronic[8,10] and lattice[8,9] properties of metals and alloys with narrow peaks near E_F.

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