Solid State Communications, Vol.32, pp.735-738.
Pergamon Press Ltd. 1979. Printed in Great Britain.

ELECTRON PHASE TRANSITION IN TiNi?

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(Received 26 July 1979 by V.M. Agranovich)

The optical and X-ray photoelectronic spectra and temperature dependence of magnetic susceptibility are investigated. It is found that at martensitic transformation in TiNi electron redistribution occurs which is accompanied by cardinal change of Fermi surface. Based on the data obtained in B2-structure (CsCl) E_F is assumed to lie in the kT-vicinity of the N(E) peak that determines the tendency to the structural instability of B2.

1. Introduction

Wang [1] suggested that martensitic transformation (MT) in TiNi was the electron phase transition from a "metallic" closepacked B19-structure to "covalent" B2. This assumption was further developed in [2] where the MT model was proposed according to which the MT in TiNi was performed by shift and empting of the s-band that was accompanied by change of the d-band width and the 1.1ev Fermi level (E_F) shift with the unchanged form of density of states (DOS). In [3] by soft X-ray appearance potential spectroscopy it was found that the observed shift and the change of the width of unfilled portion of the d-band at MT was 0.1ev. The latter does not agree with the Wang's model [2]. But the assumption on the s-d transition at MT in TiNi based on the analysis of the transport properties is noteworthy and requires more detailed experimental check. However, from our point of view the model of MT where one should have the 1ev shift with the unchanged DOS form does not reflect real changes in the electron structure of TiNi. To varify the model of this transition we have made complex investigation including the X-ray photoelectron (XPS), optical spectra and magnetic susceptibility which may give information on both deep states of valence electrons and their states on Fermi surface of TiNi in both phases.

2. Sample Preparation

TiNi alloy of the equiatomic composition was prepared of electrolytic Ni and iodide Ti by electron-beam melting in a helium atmosphere. For the alloy homogenization the sixfold melting was used. The composition of the alloy was determined from the weight of the elements Ti and Ni and the ingot, respectively. The samples were annealed at 800°C for 2 hours and thereafter slowly cooled to room temperature. B2(austenite) - B19' (martensite) martensitic transformation in TiNi alloy of this composition in the first cycles according to X-ray study occurs without rhomboidal distortion of the initial B2-structure, The temperatures of MT determined by the X-ray method are Ms = 78°C, Mf = 45°C (start and end of MT during cooling), As = 100°C, Af = 120°C(start and end of MT during heating). This is the first-order transition.

3. Results and Discussion

3.1. X-ray photoelectron spectra

XPS measurements were performed. by means of the Hewlett-Packard 5950A spectrometer with energy resolution of about 0.7ev. In the measuring chamber the pressure was about 4×10^{-9}torr. Before measurements, samples were cleaned by argon ionsputtering (V=1000v, I=30A). The purity of the surface was checked by L_{23}-line of Ti oxide. XPS measurements were repeated three times on freshly prepared surfaces.

In Fig.1 XPS spectra are presented in both phases. One can see that the forms of spectra do not significantly change at MT and display fine structures in both states. More clear division of the shoulders at energies 1.7 and 1.2ev in B2 should be noted. The main effect of MT is the narrowing of the XPS in B19' for 0.3ev (the width in B2 is 3.2 ev on half maximum) and the reduction of the high-energy slope by a factor of two. The elements of the structure at energies 0.4 and 3.3ev (in B2) shift for 0.2ev in B19 from Fermi level (which in the given case coincides with E_F of the spectrometer material).

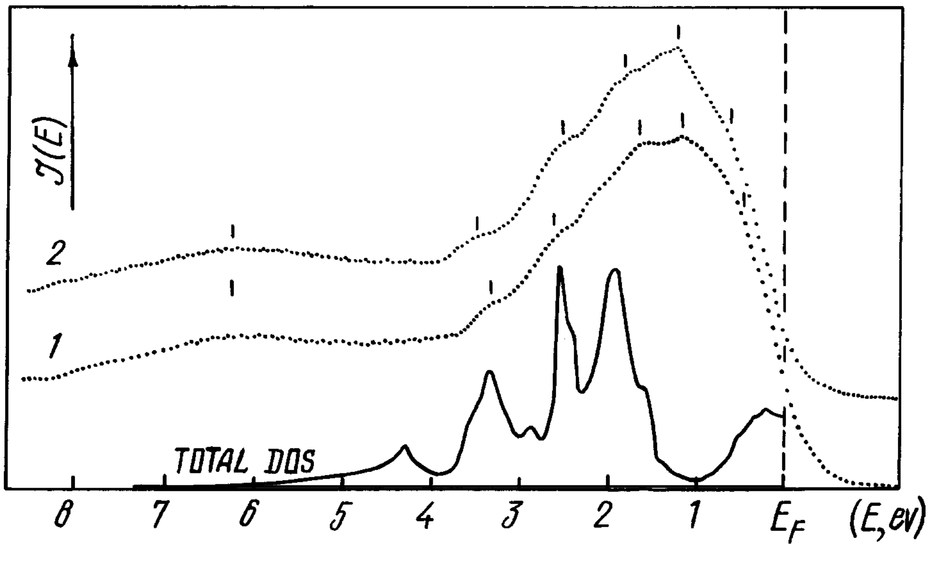

Fig.1. X-ray photoelectron spectra of TiNi in B2(1) at T=130° C and in B19'(2) structure at T=20 C, respectively (the average of three measurements); and the density of states N(E) from [4].

The comparison of XPS in B2 structure with the DOS for TiNi calculated by the selfconsistent APW method shows that the structure elements observed at energies 1.7, 2.6, 3.3 ev and 0.4ev as well may be associated with the main maxima in DOS [4]. However, in calculated DOS the bands at energies about of 1.2 and 6.2ev are not observed. From comparison of XPS with the L_3 X-ray emission spectra of Ti and Ni in TiNi [5] it follows that these bands are caused by Ti d-states. The XPS narrowing with almost unchanged d-band shape at MT shows the decrease of the d-electron number in martensite.

The smoothing of a weak gap dividing the shoulders at energies 1.2 and 1.7ev is apparently connected with decrease of the d-subbands localization degree in B19' that is in agreement with the d-electron number decrease. The high-energy edge intensity lowering indicates the decrease of DOS at E_F. The displacements of some structure elements at MT for 0.2ev relative to E_F enable one to conclude that if E_F shift occurs at MT it must not be more than 0.2ev. The latter is in agreement with the results [3] and shows that the Wang's model cannot be applied for the B2-B19' transformation in TiNi description.

3.2. Magnetic susceptibility

Temperature dependence $\chi(T)$ was studied in [1]. The absence of visible change of χ at the stage preceeding direct MT it was concluded that temperature independent magnetic susceptibility occurred in TiNi. In this paper temperature dependence χ (T) in B2-structure at 80-400°C, in B19'-structure at 12-100°C and in the MT region was investigated by Faraday's method. The obtained results are given in Fig.2. It is seen that χ depends on temperature in both structures. The points of strong changes of χ (T) coincide with the characteristic temperatures defined by the X-ray method. The χ (T) slope has a different sign in both phases. It is known that the slope sign of χ (T) is determined by the E_F position with respect to the extrema of DOS [6]. The positive slope will occur if E_F is in minimum, and negative if E_F is in maximum of N(E). From this fact it follows that in the structures B2 and B19' E_F is in the region of maximum and minimum of N(E), respectively.

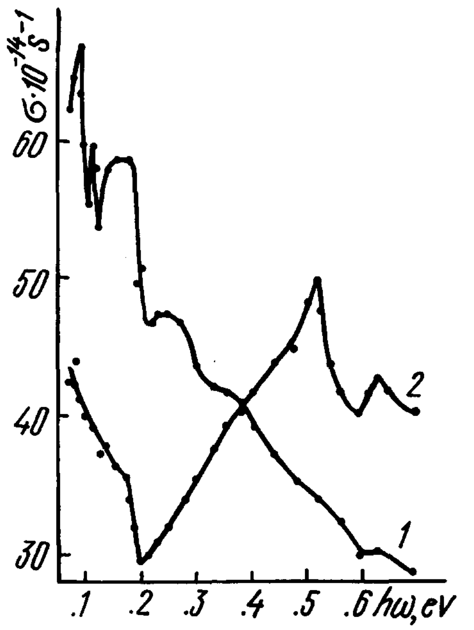

Fig. 2. Temperature dependence of the TiNi magnetic susceptibility.

On the assumption of the unchanged diamagnetic contribution the decrease of χ in B19' by a factor of two is caused by both spin- and orbital susceptibility decrease that may be associated with the decrease of d-electron contribution to density of states at E_F. This is in agreement with the XPS data given above.

Based on these results, on the assumption of the main contribution to electrical resistance from s-d scattering one can understand the character of the TiNi electrical resistance change at MT. The observed decrease of ρ in martensite ($\rho_{B19'}/\rho_{B2}$ = 0.8) is connected with the decrease of s-d scattering.

3.3. Optical Investigations

The optical constants n and k were obtained by polarimetric Beattie method in the energy range 0.07-5ev. It is found that only an ifra-red (IR)part (0.07-0.8ev) is sensitive to MT. This part will be discussed here. In more detail these results and the investigation method were presented in [7].

Figure 3 shows optical conductivity $\sigma(\omega)$= nkν in both phases. One can see that IR of optical conductivity which is stipulated by an electron transition in the Fermi-level region changes cardinally at MT. In austenite $\sigma(\omega)$ increases continuously with energy reduction displaying peaks of the interband absorption (0.085, 0.113, 0.17,0.24, 0.34ev) which do not allow the contribution from free carriers on the Fermi surface to be separated out. In martensite the absorption edge shifts to higher energies where a new strong peak appears near 0.52ev. The growth of σ at $\hbar\omega <$ 0.2ev is caused by free carriers of the Drude-Zinner type.

The strong interband absorption in IR of σ in austenite shows high DOS in the kT vicinity of E_F. (However, some peaks can be associated with many-body effects). The extinction of these bands and the appearance of a strong peak at 0.52ev are connected with the fact that E_F gets into the gap which may occur from any degenerate states splitting in the high-symmetry points of the Brillouin zone. In the band structure calculation [8] of TiNi the states (Γ_{12} , $X_{5'}$) which could be splitted in the rhombic symmetry lattice B19' are 0.5ev higher over E_F and form the N(E) peak there [9]. The same peak but sharper (the width 0.05ev) is in selfconsistent calculation of N(E) [4]. The strong interband absorption in far IR and also the observed temperature dependence of magnetic susceptibility can be understood if E_F lies in the kT vicinity of this peak. Such E_F position in TiNi provides the tendency to structural transformation as it occurs in A-15 compounds [10].

From this point of view one can understand the data on decrease of the temperature of the MT start M_s with alloying [11,12] or cycling. Admixtures and lattice defects cause d-electron scattering which results in excitation lifetime decrease and N(E) peak smoothing.

It should be noted that the gap around E_F in martensite only tentatively stabilizes the structure. It follows from magnetic susceptibility data that the change rate of χ is 0.1 units per degree in B19', that indicates a very steep gap edges. Lomer noted that such an extremal position of E_F in the vi-

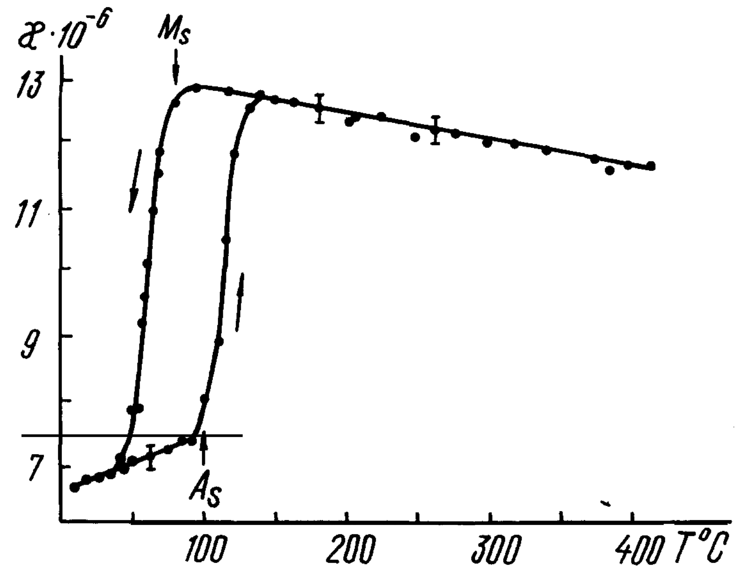

Fig.3. Infra-red optical conductivity in B2(1) at T=130°C and in B19'(2) structure at T=20°C.

cinity of sharply varied DOS may cause structural instability[13], which is probably realized with further cooling of TiNi, where, according to [14], phase transition (monoclinic-threeclinic martensite) close to the second-order phase transition occurs.

Thus, the observed variations of an electron structure indicate the decrease of localization degree of valence electrons and the essential reconstruction of the TiNi Fermi surface at B2-B19'MT. However, based on this data can this first-order pronounced transition be considered as an electron transition?

Acknowledgements - We thank D.A. Papaconstantopoulos for the communication of unpublished results of band-structure calculations.

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