Effect of temperature on the x-ray photoelectronic spectrum of the valence electron of an Fe-Ni alloy of Invar composition

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(Submitted June 8, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 5, 276–278 (5 September 1976)

PACS numbers: 79.60.Cn, 71.30.Hr

An earlier investigation[1] of the scattering of x rays from an Fe-Ni alloy of Invar composition has revealed that when the temperature is raised from 78 to 500 °K the atomic factor decreased by approximately 1.4%. It was therefore of interest to trace the energy-dependent variations in the valence band of Invar when the temperature is raised.

An HP-5950A photoelectronic spectrometer was used to investigate the spectra of the valence electrons in an Fe-Ni alloy containing 35.8 at.% Ni. The impurity concentration did not succeed 0.1 wt.%. Investigations were made at 122, 300, 450, 500, and 580 °K. The Curie temperature of this alloy is 520 °K.[2]

Prior to plotting the spectra, the samples were mechanically cleaned in a nitrogen-gas atmosphere of increased purity and etched by argon ions in the sample-preparation chamber. The argon pressure in the chamber was 5×10^{-5} Torr. The accelerating voltage of the ion gun was 500 V and the cleaning time was 10 min. The degree to which the samples were rid of the oxides and the hydrocarbon layers was monitored against the O 1*s* line of oxygen and the C 1*s* line of carbon. As a result of the purification no noticeable peaks were observed in the course of the investigation of the sample surface in the binding-energy regions of the O 1*s* and C 1*s* electrons. The vacuum in the working chamber at a sample temperature 300 °K was not worse than 2×10^{-9} Torr.

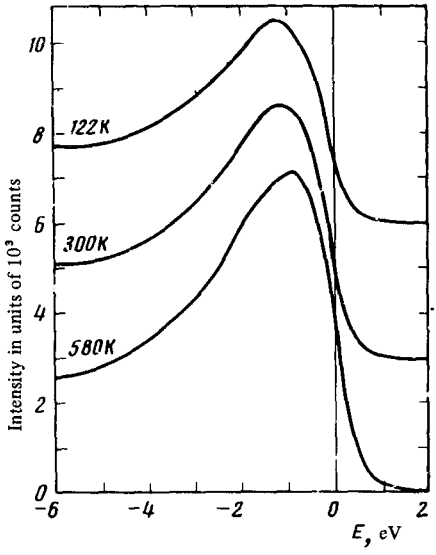

FIG. 1. X-ray photoelectron spectra of valence electrons at 122, 300, and 580°K.

Figure 1 shows the spectra of the valence electrons of the Invar. A change in temperature causes a certain change in the position of the maximum and in the shape of the valence band. These changes are illustrated in Fig. 2. When the sample is heated from 122 to 580°K, the peak shifts towards lower binding forces by approximately 0.36 eV. The asymmetry index[1)] also change with rising temperature. When the sample was heated from 122 to 580°K, the asymmetry index decreased respectively from 0.43 to 0.32.

Owing to the electric contact, the position of the Fermi level of a metallic sample in a photoelectronic spectrometer coincides with the Fermi level of the spectrometer. The change of the position of the Fermi level in the 3*d* band of the sample is thus revealed by the shift of the spectrum relative to the Fermi level of the spectrometer. A shift of the sample Fermi level to the right will be accompanied by a shift of the maximum of the spectrum to the left. Conse-

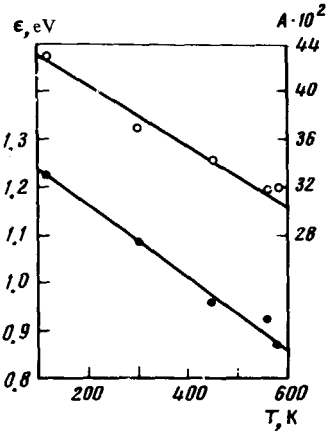

FIG. 2. Temperature dependence of the position of the maximum and of the asymmetry index of the photoelectron spectrum of the valence electrons of Invar.

quently, the shift of the maxima of the spectrum towards the Fermi level of the spectrometer, observed in our experiments with rising temperature, can be attributed to a shift of the Fermi level in the 3*d* band of the sample towards the bottom of the band.[3] This shift is accompanied by a narrowing of the long-wave part of the spectrum, which causes the observed lowering of the asymmetry index. It is known[4] that the part of the 3*d* band filled with five electrons per atom is an antibinding part up to the Fermi level. Electrons having this energy state occupy a more localized space than even in the isolated atom. These electrons are in a low-stability state and when the temperature is raised for some reason, possibly as a result of the interference of the electrons with the 4*s* electrons, they are capable of going over into a collectivized state. When the scattering of x rays is investigated, this process is accompanied by a lowering of the atomic factor.[1] Thus, the effects observed us in[1] and in the present investigation represent one and the same phenomenon in spatial and energy representations. As a result of the narrowing of the antibinding part of the 3*d* band, the interatomic coupling is strengthened. Consequently two processes take place simultaneously in an Invar with rising temperature: on the one hand the amplitude of the atom vibrations increases, and on the other hand the interatomic binding forces are increased as a result of the narrowing of the antibinding part of the 3*d* band. As a result of these two opposing processes, neutralization of the anharmonic components of the thermal vibrations of the atoms takes place within certain limits, and this determines the anomalous course of the temperature dependence of many macroscopic properties. In particular, predominance of the second process can cause the temperature coefficient of expansion to be negative, as is the case in Invars at a temperature below 60 °K.[5] Allowance for these concepts explains well also other known anomalies of the properties of Invar alloys, including the increase of the elastic constants with increasing temperature.

[1)]The asymmetry index is defined as the ratio of the long-wave part to the short-wave part at half the intensity at the maximum of the spectrum.

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[1]A.I. Zakharov, Fiz. Metal. Metalloved. **41**, 445 (1976).
[2]A.Z. Men'shikov and E.E. Yurchikov, Izv. Akad. Nauk SSSR Ser. Fiz. **36**, 1463 (1972).
[3]A.I. Zakharov, Yu.A. Matveev, and T.M. Zimkina, Izv. Akad. Nauk SSSR Ser. Fiz. **40**, 362 (1976).
[4]J. Friedel, in: Physics of Metals I, Cambridge, 1969.
[5]A.I. Zakharov and L.N. Felotov, Fiz. Metal. Metalloved. **23**, 759 (1967).