JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Metals and Alloys II

Invar-Behaviour and Magnetic Moments of the γ-Phase of Iron-Palladium Alloys

A. KUSSMANN AND K. JESSEN

Institut Berlin der Physikalisch-Technischen Bundesanstalt
Berlin-Charlottenburg, Germany

The subcooled γ-phase of the system iron-palladium shows a small thermal expansion (invar behaviour) at 30 At.%, and keeps, however,—in contrast to the nickel steels which are becoming nonmagnetic here—its ferromagnetic behaviour (4.2 Bohr magnetons per atom) nearly up to pure γ-iron. Due to the absence of a nonmagnetic neighborhood the expansion anomaly can be hardly explained here by a temperature dependent mixture ratio of ferro- and antiferromagnetic iron ions.

The invar property, i.e., anomalous thermal expansion, has been found especially in the cubic face centered phases of iron-nickel and iron-platinum. It exists in the limited ranges of concentration around 35% Ni and 25% Pt, respectively. Besides the invar property these alloys have the following common characteristics which can be seen in Figs. 1 and 2.

(a) Relatively low Curie temperature in combination with comparatively high magnetization and extremely high volume magnetostriction.

(b) Neighborhood to the region in which the γ-phase becomes unstable and changes into the α-phase with a cubic body centered lattice by a diffusionless, martensitic type transformation.

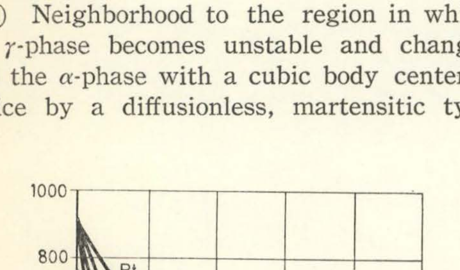

Fig. 1. Phase diagram of Fe-Ni and Fe-Pt alloys (without ordered structures).

(c) Insertion of a nonmagnetic γ-region between the α-phase and the invar-region, resulting in a steep drop of Curie temperature.

Each of these characteristics alone has been used for an attempt to explain the reason for the expansion anomaly.

The characteristic (a) has lead to a magnetic interpretation. The high volume magnetostriction due to spontaneous magnetization which, starting at the Curie point, increases with decreasing temperature counteracts the normal thermal contraction. As it is well known, this interpretation is entirely right, but still does not include the answer to the question why the high values of magnetostriction and thus the invar effect are limited to certain alloy systems only.

Earlier attempts of an interpretation of the characteristic (b) by means of the partial overlapping of the α-γ transformation and its counteracting volume expansion in the invar region have been taken up by Tino[1]. In order to circumvent the contradictions which result from the missing of α-phase in the X-ray pattern and the impossibility of a quick conversion at low temperatures, he assumes that the distribution of the α-phase particles is highly dispersed and the particles are so small that they are nonmagnetic and can not be detected in the X-ray pattern. Anyhow, these interpretations are difficult to prove experimentally, but could not be disproved as well.

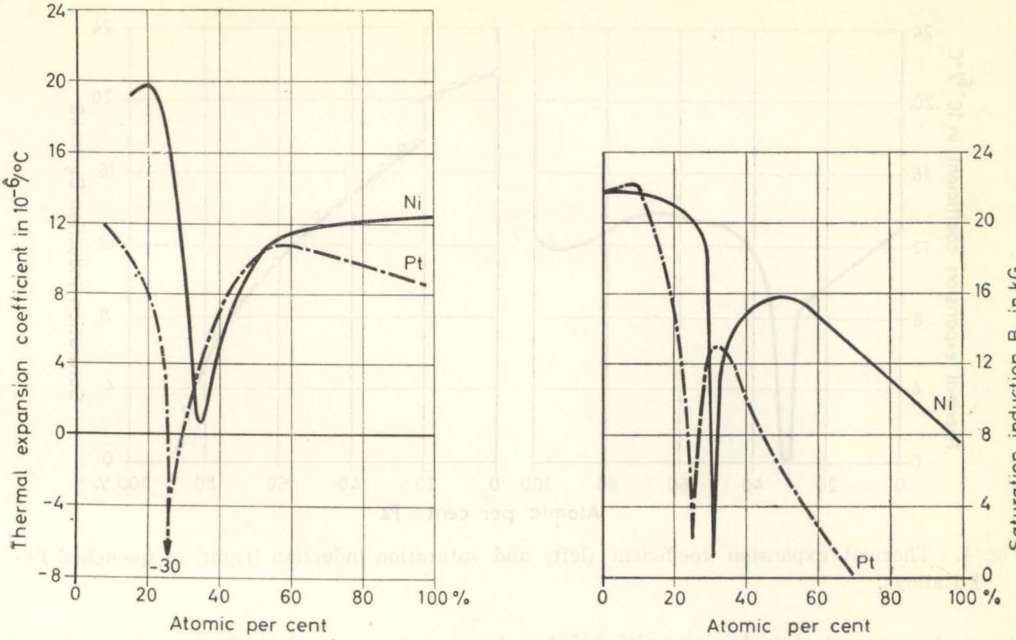

Fig. 2. Thermal expansion coefficient (left) and saturation induction (right) of Fe-Ni and Fe-Pt alloys.

The latest interpretations are based on characteristic (c) i.e., the existence of the non-magnetic region of the γ-phase in the close neighborhood of the invar anomaly. Dehlinger[2] first stressed the importance of the shift of the exchange integral towards negative values. Later Kondorsky and Sedov[3] remarked that, similar to the pure γ-iron with its nearly temperature independent susceptibility, the iron-rich austenitic nickel steels are "latent" antiferromagnetic, i.e., characterized by a negative exchange integral within very small domains of adjacent iron ions. They proved this by showing the existence of a Néel point for alloyed austenitic steel. Further, they assume that this antiferromagnetic behaviour does not end at 25 or 28% Ni, but extends into the invar region. In this case the mixture ratio of ferro- and antiferromagnetic domains could be influenced by pressure and temperature changes, and this behaviour is therefore the reason for the invar effect.

In order to contribute to the clarification of the problem, binary alloys of the iron and platinum metals were again examined with respect to their invar behaviour. There has been found no invar effect in the systems iron-iridium, -rhodium and -ruthenium; on the other hand it has been found in the system iron-palladium under a certain heat treatment. In the equilibrium state, i.e., for slow cooling or after a long time warming, there are the ordered phases, FePd and $FePd_3$, and the heterogeneous field between FePd and α-iron which does not show any remarkable expansion behaviour. By quenching, however, one can suppress the formation of the super-

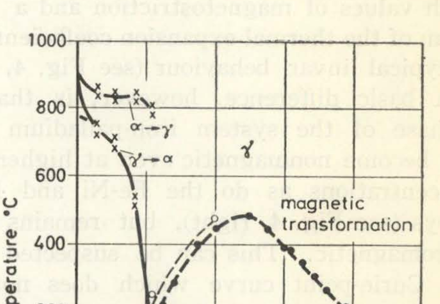

Fig. 3. Metastable structural fields in rough quenched Fe-Pd alloys.

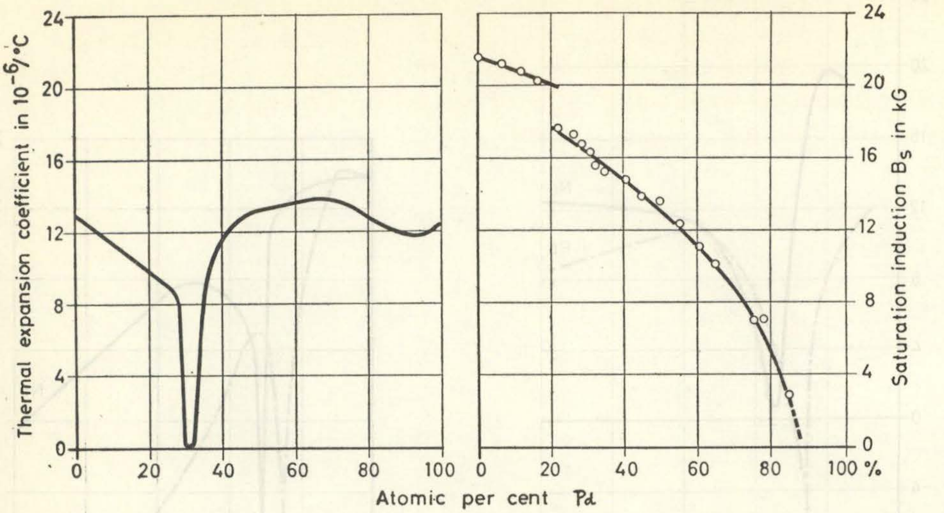

Fig. 4. Thermal expansion coefficient (left) and saturation induction (right) of quenched Fe-Pd alloys.

structure phases and the decomposition into the components, FePd and α-iron. By this procedure one gets the γ-phase of the non-equilibrium Fe-Pd alloys corresponding to that of the system iron-nickel (compare Fig. 3). Starting from the A_3 point of iron the α-γ transformation temperature decreases with increasing Pd-content, and reaches room-temperature at about 28 At.% Pd. The Curie-points of the disordered γ-phase lie on an arc-like curve.

In this subcooled γ-phase, there exists, entirely analogous to the iron-nickel alloys, high values of magnetostriction and a minimum of the thermal expansion coefficient, i.e. a typical invar behaviour (see Fig. 4, left).

A basic difference, however, is that the γ-phase of the system iron-palladium does not become nonmagnetic even at higher iron concentrations as do the Fe-Ni and Fe-Pt alloys (see Fig. 4, right), but remains fully ferromagnetic. This can be suspected from the Curie-point curve which does not decrease so steeply to low temperatures but rather slowly. The difference between the two groupes of systems becomes evident by comparision of the behaviour of the saturation magnetization. Fig. 4 (right) shows that, in contrast to the Fe-Ni and Fe-Pt alloys, the magnetization of the γ-phase of Fe-Pd alloys in the intermediate concentration range has no drop despite of decreasing Curie-temperature. The values increase in direction to pure iron, so that there appears nowhere a zero point of magnetization but only a small jump by going over from γ- to α-alloys.

A striking proof for the ferromagnetic character of the γ-phase seems to have been established by susceptibility measurements at high temperatures. The susceptibilities of the γ iron-nickel alloys show the small temperature dependence, characteristic for antiferromagnetism, up to 20 At.% Ni. On the other hand, even a small addition of palladium (approx. 7%) changes the behaviour of γ-iron to that of ferromagnetic substances above the Curiepoint. This can be seen from the fact that it follows the Curie-Weiss law with positive Curietemperatures, as can be seen clearly in Fig. 5. The extrapolated θ-values lie at positive temperatures and join

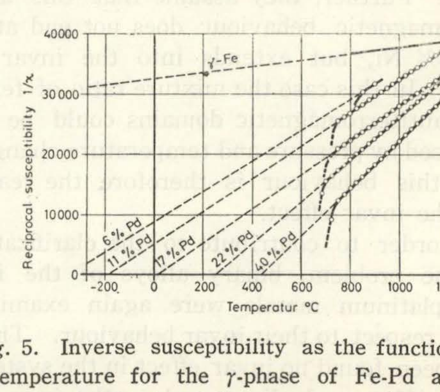

Fig. 5. Inverse susceptibility as the function of temperature for the γ-phase of Fe-Pd alloys (measurements by rising temperatures).

very well to the curve which has been measured directly in the accessible ferromagnetic region. The magnetic moment of the iron-rich γ-phase with Pd concentrations above 7% Pd has been calculated to be 4.2 Bohr magnetons per atom.

One must conclude that the iron-rich γ-phase of Pd alloys should be ferromagnetic at sufficiently low temperatures if they were stable at these temperatures. There is no indication for an antiferromagnetic coupling in the subcooled γ-phase in the immediate neighborhood of the invar alloys. Consequently, the characteristic (c) mentioned above seems to be no necessary condition for the existence of an invar effect.

References

1 Y. Tino: J. Sci. Res. Inst. **47** (1952) 141.
2 U. Dehlinger: Z. Metallkunde **28** (1936) 194.
3 E. I. Kondorsky and V. L. Sedov: J. Appl. Phys. **31** (1960) 331S.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Paramagnetic Susceptibility of Some b.c.c. Transition Element Alloys and Its Temperature Dependence

S. TANIGUCHI*, R. S. TEBBLE AND D. E. G. WILLIAMS
University of Sheffield, England

The paramagnetic susceptibilities of some b.c.c. transition metal alloys have been measured in the temperature range between 20° and 1350°C. The observed curve of χ_{20} (the room temperature susceptibility) against q (number of outer $d+s$ electrons) has been found to be binodal and similar for the first, second and third series alloys. The susceptibility is a maximum for $q\sim5$ and a minimum at slightly less than 6. The temperature dependence of susceptibility for alloys measured is as expected from the band model assuming that the shape of the density of state curve follows the $(\chi_{20}-q)$ curve.

The susceptibility and its temperature dependence of the h.c.p. phase have been found to be quite different from those of the b.c.c. phase of the same composition. A possible shape for the density of state curve of the close packed structure is also proposed based on the present study and the available data.

The paramagnetic susceptibilities of b.c.c. Ti-V, V-Cr, Cr-Mn (up to 50% Mn), Zr-Nb, Nb-Mo, Hf-Ta, Ta-W, Ta-Re (up to 37.5% Re) and Nb-Ta alloys have been measured in the temperature range 20° to 1350°C by means of a Sucksmith ring balance.[1] Most of the raw materials used for the preparation of the alloys were the spectrographically standardized substances supplied by Johnson, Matthey and Co., and they were melted in an argon-arc furnace. Except for Ta-Re and Nb-Ta alloys, these alloys are the solid solutions of neighboring transition elements in the same series in the periodic table.

The observed room temperature suscepti-

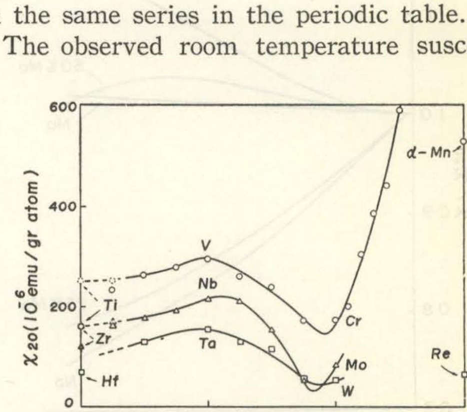

Fig. 1.

* On leave from the Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.