crystal, as well as the polariton anharmonicity parameters $\gamma(\omega)$ and $\Delta(\omega)$.

The authors thank V. M. Agranovich for interest in the work and T. E. Abramovich for her many computer calculations.

Frequency dependence of the function $\gamma(\omega)$ in a GaP crystal. Points: [experi]mental values; 1) calculation from Eq. (13) assuming $\Delta(\omega) = 0$; 2) [calcula]tion from Eq. (13) with $\Delta(\omega) \neq 0$.

...) (Fig. 4) increases monotonically with the frequency, [with]out singularities, the curve of $\gamma(\omega)$ (Fig. 5) has two [maxi]ma, at about 340 and 355 cm^{-1}. Two maxima are also [found] in direct measurements[6] of $\gamma(\omega)$, but the second of [these] is closer to the first, at about 345 cm^{-1}. Our direct [mea]surements of $\gamma(\omega)$ in the ω space are in satisfactory [agre]ement with our results from measurements in k space [(the] points in Fig. 5). The difference between our results [and] those in Ref. 6 seems to be due to a difference in qual-[ity of] the GaP crystal.

Thus, by means of the proposed photoelectric method [of] measuring linewidths for Raman scattering by polari-[tons] in the k space of a GaP crystal, we have found the [frequ]ency dependences of the absorption coefficient $\alpha(\omega)$ [and the] imaginary part $\varepsilon''(\omega)$ of the permittivity of the

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Translated by J. B. Sykes

Effect of hydrogen pressures up to 20 kbar on the Curie point of Fe–Ni Invar alloys

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The behavior of the electrical resistance and Curie point of alloys containing 32.5 and 36 at.% Ni was measured at pressures up to 20 kbar in both an inert medium and in a hydrogen atmosphere. It was found that the value of dT_C/dP, which was pressure-independent in an inert medium, increased with increasing hydrogen pressure and became positive at $P \sim 15$ kbar. It was shown that this effect is due to the dilatation of the Invar lattice as a result of incorporation of hydrogen.

PACS numbers: 75.30.Jy, 75.80.+g, 62.50.+p

[It] was shown in Ref. 1 that the $\gamma_1 \rightleftarrows \gamma_2$ equilibrium [...]s (where γ_1 and γ_2 are the hydrogen-poor and hydro-[gen-ri]ch phases of an interstitial solid solution based on [the] metal lattice) on the T−P diagrams of alloys in the [F]e−H system terminate at critical points for an iron [conten]t $\lesssim 40$ at.% and that increasing iron content causes [the cri]tical temperature to decrease from $\approx 325°$C for an [alloy w]ith 5 at.% Fe (Refs. 1 and 2) to room temperature [for an a]lloy with 40 at.% Fe (Refs. 1 and 3).

[Th]is paper reports the results of a further investiga-

tion of the Ni−Fe−H system. The electrical resistance and Curie points of two alloys, containing 32.5 and 36 at. % Ni, were measured at pressures up to 20 kbar in both an inert medium (silicone oil) and in an atmosphere of hydrogen. Alloys of these compositions were chosen for the following reasons.

a) According to the results of Ref. 1, the values of the hydrogen concentration in the Fe−Ni−H solutions formed under pressure correspond to regions on the T−C diagrams which are far from the domes of the separation

into phases γ_1 and γ_2. The hydrogen concentration in the solution must increase slowly and smoothly with increasing pressure, and this will lead to a monotonic pressure dependence of the electrical resistance, which is weak compared with changes at the $\gamma_1 \rightarrow \gamma_2$ transitions. A check of this last assertion was all the more desirable, because appreciable (~30%) anomalies of the resistance were found in Ref. 3 for alloys of similar composition at hydrogen pressures of 15 kbar at room temperature.

b) At atmospheric pressure, the range of existence of fcc solutions (γ phase) on the $T-N$ diagram of the Fe–Ni system is bounded for low Ni concentrations by a martensitic transformation to the bcc α phase. The temperature of the $\gamma \rightarrow \alpha$ transformation rises to room temperature when the nickel content is reduced to ≈ 28 at.% (Ref. 4). Hence, the alloys investigated here, together with those studied in Refs. 1 and 2, effectively cover the whole range in which the γ-phase Fe–Ni solutions are stable under normal conditions.

c) Finally, alloys with 32.5 and 36 at.% Ni belong to the Invar series, which are interesting because of the anomalously strong pressure dependences of many physical properties (particularly the magnetic properties).[5,6]

The alloys were made by melting together electrolytic Ni and carbonyl Fe in an induction furnace in an argon atmosphere. The ingots were homogenized by annealing at 1100°C for 100 h, followed by quenching in water. Samples were prepared from a foil 0.05 mm thick. The pressure was measured by a manganin wire gauge with an accuracy of ± 0.2 kbar and ± 0.4 kbar in the inert medium and in the hydrogen atmosphere, respectively; the temperatures were measured by a Chromel–Alumel thermocouple with accuracies which were respectively ±1°K and ± 3°K. The Curie points T_C were determined to ± 3°K by a differential transformer method from the curves of the temperature dependence of the initial magnetic susceptibility.[7]

The isothermal pressure dependences of the electrical resistance in an inert medium (curve 1) and in hydrogen (curve 2) for an alloy containing 32.5 at.% Ni are presented in Fig. 1. The measurements were made at 250°C, which was ~100°C above the Curie temperature for this alloy at atmospheric pressure. The curves were obtained as follows: The pressure was changed in steps of 1–3 kbar, and then the electrical resistance was measured at a fixed pressure. In an inert medium the value of the resistance was established as soon as the pressure had been fixed and was then independent of time. In the hydrogen atmosphere there was a time dependence of the resistance $R = R(\tau)$ after the pressure was changed, and this was a consequence of the diffusion process by which an Fe–Ni–H solid solution is formed. At the measurement temperature of 250°C this dependence reached saturation after $\Delta\tau \sim 10$ min, and therefore the sample was held at constant pressure for 30
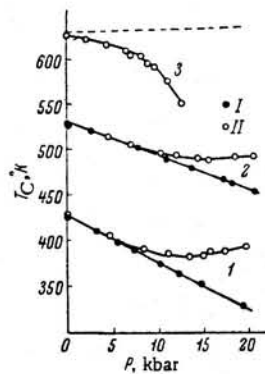
FIG. 2. Curves $T_C = T_C(P)$ ... with Ni concentrations (at. 32.5; 2)36; 3)100. I) in a ... dium; II) in a hydrogen atmosp... The dashed line shows the depe... $T_C = T_C(P)$ for Ni in an inert me...

min and we plotted the limiting value of resistance corre... sponding to the equilibrium hydrogen concentration under these conditions.

The resistances in an inert medium and in hydrogen should of course coincide at atmospheric pressure, be... cause of the low solubility of hydrogen in Invar alloys. The discrepancy between the initial values of the resistance in Fig. 1 is due to the irreversibility of the resistance changes in a hydrogen atmosphere (curve 2 was measured for decreasing pressure). In order to avoid confusion, we do not show the curve $R = R(P)$, which was obtained for increasing pressure in a hydrogen atmosphere and which starts from the same point as curve 1.

We note that the change in the electrical resistance with hydrogen pressure in the Invar alloys which we investigated is one or two orders less than that found for the $\gamma_1 \rightarrow \gamma_2$ transformation in Ni–Fe alloys with less Fe (Refs. 1 and 3), which shows that there is no $\gamma_1 \rightarrow \gamma_2$ phase transformation of the first kind (in the $T-P$ range studied) in the alloys with more than 40 at.% Fe (Ref. 1). The anomalies of the electrical resistance of Invar alloys at room temperature, found in Ref. 3, were evidently a consequence of the fact that these alloys initially contained two phases. They were in the form of films 5–10 μ thick, and for these film thicknesses of Invar alloys it is quite possible for an appreciable amount of the α phase to be formed when the quench from a high temperature is not sufficiently rapid, because — although the temperature of the $\gamma \rightarrow \alpha$ transformation is below room temperature for these alloys — at room temperature these compositions correspond to a two-phase region ($\alpha + \gamma$) on the equilibrium $T-C$ diagram.

The pressure dependence of the Curie temperature of our Invar alloys in both an inert medium and in hydrogen is presented in Fig. 2 (for convenience of comparison with the literature the temperature is given in degrees Kelvin). The alloys with 32.5 and 36 at.% Ni, which had Curie points at 426.5 and 530°K, respectively, at atmospheric pressure, showed a linear decrease in the Curie point with pressure in an inert medium at a rate (dT_C/dP) equal to -5.05 ± 0.10 and -3.7 ± 0.1°K/kbar, respectively, which is in good agreement with the results of Ref. 6. Just as in the measurements of the electrical resistance, we observed a time dependence of the Curie point in a hydrogen atmosphere after the pressure was fixed, and saturation was reached after $\Delta\tau \sim 30$ and 10 min for the compositions 32.5 and 36 at.% Ni (this difference between the saturation times was mainly due to the different temperatures at which the Fe–Ni–H solid solutions are formed near the
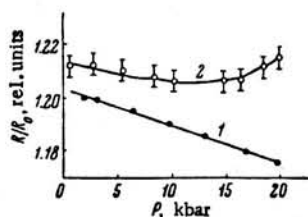

FIG. 1. Pressure dependences of the electrical resistance at 250°C of a sample containing 32.5 at.% Ni: 1) in an inert medium; 2) in a hydrogen atmosphere. Here, R_0 is the sample resistance at 1 bar and 20°C.

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Composition, at. % Ni	ΔT_C, °K (P = 20 kbar)	ΔV_{calc} (Å)³ (P = 20 kbar)	ΔV_0 (Å)³	ΔV_{exp} (Å)³	$\eta_{exp} \cdot 10^2$	$\eta_{calc} \cdot 10^2$
36	41	0.5	0.75±0.20	0.8±0.2	5.1±0.2	6.6
32.5	71	0.6	0.65±0.20	0.8±0.2	4.1±0.2	5.7

corresponding Curie temperatures). The diagram shows the values of T_C after the samples had been held at a fixed hydrogen pressure for 90 and 30 min, respectively.

It is seen from Fig. 2 that above $P \sim 10$ kbar, $T_C = T_C(P)$ in a hydrogen atmosphere shows an increasing deviation from the corresponding curve measured in an inert medium, and at $P \sim 20$ kbar the Curie point even begins to rise increasing hydrogen pressure.

We note that the Curie points of Ni (Fig. 2) and of γ-Fe alloys with ≤ 15 at.% Fe (Ref. 1) decrease with increasing hydrogen pressure. The opposite sign of this effect in our alloys is clearly associated with the anomalies of Invar alloys, and in particular with the anomalously strong volume dependence of the Curie point; hydrogen, which forms an interstitial Fe−Ni−H solid solution, dilates the crystal lattice of the alloy. Let us estimate the size of this effect. We shall regard the difference between the values of T_C of Invar alloys in a hydrogen atmosphere and in an inert medium at a given pressure, i.e., $\Delta T_C(P)$, as a consequence of the increase in T_C due to the dilatation of the unit cell of the Fe−Ni alloy when hydrogen enters into it interstitially. Then

$$\Delta V(P) \approx \frac{\Delta T_C(P)}{\left(\frac{dT_C}{dV}\right)_P} \approx -\frac{kV}{\left(\frac{dT_C}{dP}\right)_{in}} \Delta T_C(P), \tag{1}$$

here V is the volume of the unit cell of the Fe−Ni alloy; $\Delta V(P)$ is the difference between the unit cell volumes in hydrogen and in an inert medium; k is the compressibility of the alloy.

The validity of the approximate relation (1) is supported by the results of Ref. 8, where it was shown from measurements on ternary Fe−Ni−Cu and Fe−Ni−Mn alloys that the value of $(dT_C/dP)_{in}$ for Fe−Ni Invar alloys is mainly determined by the iron concentration.
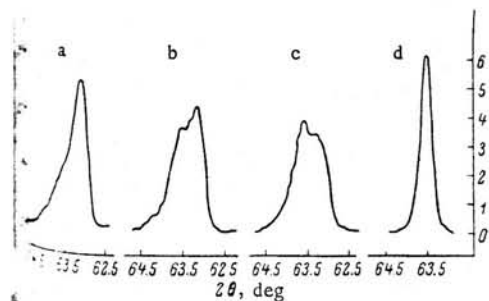

Diffraction curves for the (200) line of a sample with 32.5 at. % Ni saturated with hydrogen at P= 20 kbar and T = 250°C (a-c), and for a sample containing no hydrogen (d). a) 20 min after the sample was taken from liquid nitrogen; b) 35 min after removal; c) 50 min after removal. The diffraction curves were measured at T ≈ 30°C, using Fe Kα radiation.

The values ΔV_{calc} calculated from Eq. (1) at P =20 kbar are given in Table I. The values of V and k are taken from Refs. 9 and 10. The volume change of the unit cell $\Delta V(P)$ which appears in Eq. (1) can also be estimated in another way. Let $\Delta V_0(P)$ be the volume difference between the unit cells at atmospheric pressure and room temperature for two alloys, one of which has a hydrogen concentration which is the same as at pressure P and T $\sim$ $T_C(P)$, while the other contains no hydrogen. Then, neglecting the difference between the compressibilities and linear expansion coefficients of the samples with and without hydrogen, we obtain

$$\Delta V(P) \approx \Delta V_0(P) + 3\alpha_T V \Delta T_C(P), \tag{2}$$

where α_T is the linear expansion coefficient of the alloy for T $\sim$ T_C.

We determined the value of ΔV_0 (20 kbar) experimentally. Samples were maintained in hydrogen for 2 h at P= 20 kbar and T =250°C, and then they and the high-pressure chamber were cooled to T= −30°C. At this temperature the pressure was lifted and the samples were removed from the chamber and placed in liquid nitrogen.[3] The change in the lattice parameter of the samples due to the interstitial hydrogen was deduced from the shift of the (200) line at 30°C, using a URS-50IM diffractometer with a beam diameter ~4 mm and Fe Kα radiation. The diffraction curves for the sample with 32.5 at. % Ni are given in Fig. 3. We note an interesting feature of the decomposition of the Fe−Ni−H solid solution at atmospheric pressure; the diffraction curves for the (200) line do not shift as a whole with time (as would be expected for hydrogen depletion homogeneous over the sample volume), but they split into parts, one of which corresponds to the lattice parameter of a solution saturated with hydrogen (Fig. 3a), while the other corresponds to a solution containing no hydrogen (Fig. 3d). It follows that the evolution of hydrogen occurs via a two-phase decomposition of the solid solution: The sample splits up into microscopic volumes, and the release of hydrogen from these is clearly controlled by the state of their surface (see also Ref. 11).

The values of ΔV_0 (P =20 kbar) and the values of ΔV_{exp}(P =20 kbar) calculated from Eq. (2) are given in Table I. The values of α_T were taken from Ref. 12. It is clear from Table I that ΔV_{calc} makes the major contribution to ΔV_{exp}. Hence, the increase in the lattice parameter when hydrogen enters the lattice interstitially plays the dominant role in Invar alloys and thus, $\Delta T_C(P) > 0$, in distinction to Ni and Ni−Fe alloys with low iron concentrations, for which the Curie point is only weakly volume-dependent [$(dT_C/dP)_{in} \sim 0.1$°K/kbar from Ref. 6] and the main effect of dissolved hydrogen is associated with the increased electron density in the 3d band (which lowers[13] T_C).

For some of the samples saturated with hydrogen, prepared as for the determination of $\Delta V_0 (P = 20$ kbar), we measured the hydrogen content by the method described in Ref. 14. The hydrogen evolved on the decomposition of the Fe−Ni−H solid solution was used to displace silicone oil from a graduated measuring cylinder at atmospheric pressure. The kinetics of this process are rather slow at room temperature; the hydrogen continued to be evolved for about three days. The results are given in Table I as n, the atomic hydrogen−metal ratio. We also quote the value n_{calc} calculated from the empirical formula

$$\frac{\Delta V_0}{n} = 11.4, \tag{3}$$

where ΔV_0 is expressed in cubic angstroms for our values of $\Delta V_0 (P = 20$ kbar). It was shown in Ref. 15 that this expression describes satisfactorily the experimental results for all previously studied fcc metals and alloys with $n < 0.7$.

It is clear from Table I that there are no large deviations from Eq. (3) for Invar alloys, although it is well known that these have anomalous P−V−T relations which distinguish them from other fcc alloys. The validity of Eq. (3) for these alloys is thus additional confirmation that the value of $\Delta V_0/n$ is, to a first approximation, determined only by the lattice symmetry of the d-band metal. This is associated with the fact that, at low concentrations, hydrogen is in the same state in all the fcc d-band metals which have been studied; in particular, it occupies interstitial sites of the same type [in a number of systems such as Pd−H (Refs. 16 and 17), Au−Pd−H (Ref. 18), and Ni−H (Ref. 19), it has been shown that these are octahedral sites), and it has the same effective radius.

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Translated by M. G. Priestley