Neutron diffraction investigation of the atomic magnetic structure of iron-nickel Invars

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The inhomogeneity of the magnetic structure of iron-nickel Invars determines the singularities of the behavior of many physical properties of these alloys, and in particular the concentration and temperature dependences of the average atomic magnetic moment \( \mu \). However, the character of the inhomogeneity has not yet been determined uniquely, and this makes it very difficult to solve the problem of Invars. Most proposed magnetic models of Invar alloys connect the magnetic inhomogeneity with the existence of long-range or short-range antiferromagnetic order in the Invars. Since iron-nickel alloys containing more than 20\% Ni (we use atomic percentages throughout) are ferromagnetic in the \( \gamma \) phase, the question arises of the coexistence antiferromagnetic and ferromagnetic orders in these alloys.

The possibility of the existence of long-range antiferromagnetic order in Invars follows from the antiferromagnetic structure of \( \gamma - Fe \) \(^{11} \) and of alloys based on iron and nickel with large content of Mn \(^{21} \) or Cr \(^{31} \) at a nickel concentration 15–20\%. Neutron diffraction has revealed in all three cited studies the same type of antiferromagnetic structure, but with different Neel temperatures \( T_N \). In this connection, interest attaches to the work of Dubinin et al., \(^{14} \) who arrived at the conclusion, on the basis of a study of neutron diffraction by a polycrystalline sample of Invar composition with 37\% Ni, that long-range antiferromagnetic order exists in the alloy, with a magnetic structure of a different type and with \( T_N = 15 \, ^{0}K \).

We report here an investigation, by neutron diffraction, of the long-range magnetic order in a single crystal containing 35\% nickel. In this case, the effect of antiferromagnetic ordering should be more clearly pronounced, and the intensities of the Bragg reflections exceed by at least two orders of magnitude the corresponding values obtained with a polycrystal having the same composition. Simultaneously, using small-angle magnetic scattering of neutrons by polycrystals, we investigated the concentration and temperature dependences of the parameters of the magnetic inhomogeneities of the ferromagnetic matrix. The combination of two-neutron-diffraction methods that differ appreciably from each other in resolution yields direct information on the magnetic structure of the Invars.

1. MEASUREMENT PROEDURE AND SAMPLES

Small-angle magnetic diffuse scattering of neutrons from polycrystals quenched from 1000 \(^{0}C \), with natural isotopic composition, was investigated with a neutron diffractometer at \( \lambda = 1.59 \, \text{Å} \) in the interval 0.1 \( < S < 1.0 \) \((S = 4\pi \rho \sin \theta, \) where \( \theta \) is the wavelength of the neutrons and \( 2\theta \) is the scattering angle). The samples had strictly the same dimensions (cylinders of 7 mm diameter and 60 mm height) and contained from 40 to 32\% nickel. The total impurity content in the alloy did not exceed 0.1\%. All the samples were investigated in the temperature interval from 90 \(^{0}K \) to the appropriate Curie temperature \( T_C \) of each alloy. Since no martensitic transformation was observed in a sample with 32\% Ni even at 4.2 \(^{0}K \) (owing apparently to the Mn and Si impurities), this alloy was investigated starting with 4.2 \(^{0}K \).

The intensities of the small-angle magnetic scattering of the neutrons were obtained by subtracting the scattering of an iron-nickel sample with 55\% Ni from the intensities of the scattering of Invar samples after suitable normalization of the experimental curves at \( S > 0.6 \). At practically equal amplitudes of the nuclear scattering of Fe and Ni, one subtracts in this manner all types of nuclear scattering, magnetic multiple scattering, and magnetic scattering due to the short-range atomic order which is preserved in the quenched alloys. \(^{15} \) The latter type of scattering is accounted for in the cross section for the diffuse magnetic scattering by interpolation of the data of \(^{16} \). Scattering from a standard vanadium sample was used to calculate the magnetic cross sections for the small-angle neutron scattering.

The diffraction of the neutrons by a single-crystal sphere of 9 mm diameter with 35\% Ni was investigated by us at 4.2 and 300 \(^{0}K \) using a neutron diffractometer with \( \lambda = 1.07 \, \text{Å} \). Measurements of the neutron intensities were carried out in the directions (100) and (110) in the angle intervals \( 8^{0} < 2\theta < 40^{0} \) and \( 8^{0} < 2\theta < 55^{0} \), respectively. The sample temperatures were monitored with a gold (cobalt)—copper thermocouple.

2. MEASUREMENT RESULTS AND DISCUSSION

1. Small-angle magnetic scattering. Figure 1a shows the differential neutron-scattering cross sections as

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functions of $S$, obtained at $90 \degree K$. The steep rise of the experimental points at $S \leq 0.1$ may be due to inelastic scattering of the neutrons by spin waves, for which there exists a critical value $S_c$ that depends on $\lambda$ and is proportional to $(1 - \frac{T}{T_C})^{-1/3}$. However, the value of $S_c$ estimated analogously by Komura et al. amounts at $90 \degree K$ to $0.045 \, \AA^{-1}$ for all the investigated alloys. Just as in (7), it is assumed that the increase of the intensity at $S \leq 0.1$ is due to spin-wave damping and to the finite resolution of the apparatus.

The angular dependence of $d\sigma/d\Omega$ in Fig. 1a is typical of fcc alloys based on Ni, in which the matrix becomes magnetically inhomogeneous around the nonmagnetic impurity atoms. Then, according to Comly et al.,

$$d\sigma/d\Omega = 0.0486c(1-c)M(S),$$

where $c$ is the concentration of the impurity atoms,

$$M(S) = \int \rho(r) \exp(irS) dr,$$

and $\rho(r)$ is the deviation of the magnetic-moment density, occurring at a distance $r$ from the impurity atom. The linear dependence of $(d\sigma/d\Omega)^{1/2}$ on $S^2$ at small $S$, which is shown in Fig. 1b, indicates that $M(S)$ is described by a Lorentzian of the form

$$M(S) = M(0)/(1 + \kappa^2 S^2),$$

where $1/\kappa$ is the parameter of the perturbation dimension.

The values of $(d\sigma/d\Omega)_0$ determined from Fig. 1b at $S = 0$ and $\kappa$ make it possible to calculate the dependence of $d\sigma/d\Omega$ on $S$. The calculated curves are shown solid in Fig. 1a and agree best with the experimental points. In Table 1 are given the values of $(d\sigma/d\Omega)_0$ and $\kappa$, obtained at $90 \degree K$, while the last line shows the values at $4.2 \degree K$. The table lists only the statistical measurement errors.

The dependence of $(d\sigma/d\Omega)_0$ on the Ni concentration, given in Table 1, incorporates at $90 \degree K$ also the temperature contribution to the scattering, a contribution which is shown in Fig. 1a and agree best with the experimental points. In Table 1 are given the values of $(d\sigma/d\Omega)_0$ for $T = 0$ are also given in Table 1. As seen from this table, the temperature contribution for the alloys with 40–34% Ni are within the limits of the $(d\sigma/d\Omega)_0$ measurement error. Allowance for the Laue magnetic scattering in accordance with the data of Collins et al., increases the values of $d\sigma/d\Omega$ by 0.025–0.030 b, depending on the composition of the alloy, and is comparable with the scattering for the alloy with 40% Ni. The results obtained for this alloy, in view of the smallness of the small-angle effect and the appreciable errors in the reduction of the data, are only approximate.

The concentration dependence of $\kappa$ at $T = 0 \degree K$, obtained by extrapolating the data of Fig. 5, is shown in Fig. 2a. If it is assumed that iron-nickel alloys have in the $\gamma$ phase a critical nickel concentration $y_0$ at which $T_C = 0 \degree K$, in the range from 15 to 20%, then the concentration dependence of the investigated compositions is given by

$$\kappa = A (y - y_0)^n,$$

where $y$ is the concentration of the nickel, and $n$ ranges from 1.43 to 1.03. For weak ferromagnets near $y_0$, a value $n = 0.50$ is predicted as a criterion of magnetic homogeneity. However, the results $y_0$ have $n = 0.52$ only at $y_0 = 28\%$, and according to Kachi and Asano, this composition has $T_C = 350 \degree K$. Thus, the concentration dependence of $\kappa$ points to a unique magnetic in-

**FIG. 1.** a) Cross sections of small-angle magnetic scattering of neutrons by Invar alloys at $90 \degree K$: 1 – 32\% Ni, 2 – 34\% Ni, 3 – 35\% Ni, 4 – 36\% Ni, 5 – 38\% Ni. b) Dependence of $(d\sigma/d\Omega)^{1/2}$ on $S^2$.

**FIG. 2.** a) Concentration dependence of the reciprocal correlation-length parameter $\kappa$ at $4.2 \degree K$. b) Distribution of the magnetic-moment perturbation density.

**TABLE 1.**

<table>
<thead>
<tr>
<th>Ni content, at.%</th>
<th>b/br. atom</th>
<th>b/br. atom</th>
<th>$n$, A</th>
<th>$\kappa$, %</th>
<th>$M(0)$ b/sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.039±0.008</td>
<td>0.054</td>
<td>0.28</td>
<td>0.09</td>
<td>38±4</td>
</tr>
<tr>
<td>36</td>
<td>0.2±0.02</td>
<td>0.21</td>
<td>0.34</td>
<td>0.13</td>
<td>31±3</td>
</tr>
<tr>
<td>35</td>
<td>0.1±0.05</td>
<td>0.25</td>
<td>0.28</td>
<td>0.33</td>
<td>26±3</td>
</tr>
<tr>
<td>34</td>
<td>1.2±0.15</td>
<td>1.40</td>
<td>0.25</td>
<td>0.20</td>
<td>19±2</td>
</tr>
<tr>
<td>32</td>
<td>1.4±0.18</td>
<td>1.40</td>
<td>0.22</td>
<td>0.26</td>
<td>19±2</td>
</tr>
<tr>
<td>30</td>
<td>1.4±0.18</td>
<td>1.40</td>
<td>0.24</td>
<td>0.21</td>
<td>19±2</td>
</tr>
</tbody>
</table>

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2. Magnetic-inhomogeneity model. The linear growth of \( \frac{dv}{d\Omega} \) and \( 1/x \) with increasing concentration of the iron atoms in the alloy indicates that the perturbation of the magnetic moments of the matrix, produced by each additional impurity, does not depend on the perturbations already present. Then, taking into account the inhomogeneity dimensions estimated from the small-angle scattering of the neutrons in the Guinier approximation\(^{\text{[5]}} \) it must be assumed that either the concentration of the perturbing impurities are sufficiently small, or that a linear superposition of the individual perturbations takes place when the perturbation regions overlap.

The decrease of \( \mu_{Fe} \) as a result of the concentration fluctuations\(^{\text{[11,14]}} \) and the low content of the perturbing impurities allow us to assume that the centers of the perturbations are Fe atoms surrounded only by Fe atoms in the first coordination sphere. The concentration of these atoms are calculated with allowance for the short-range atomic order\(^{\text{[5]}} \) by the formula

\[
c = \frac{121}{N(12-N)} (y_{Fe} - x_{Fe})^{12-n}
\]

at \( N = 0 \), where \( N \) is the number of Ni atoms in the nearest environment of the Fe atom, \( x \) is the concentration of the Fe in the alloy, and \( \alpha \) is the short-range order parameter for the first coordination sphere, which is taken from\(^{\text{[5]}} \).

The calculated values of \( c \) and of the total decrease of the magnetic moment in the region of the perturbation of \( M(0) \) are given in Table 1. The magnetic moment \( \mu_{Fe} \) at the impurity iron atom is not determined by the present procedure. It is assumed that it is close to zero or that it may even had a small negative value.\(^{\text{[14]}} \) In the latter case, short-range antiferromagnetic order is produced.

Using the Fourier transformation (2) and integrating (3), we can represent the magnetic-moment perturbation density \( \rho(r) \) in the form

\[
\rho(r) = \frac{M(0)x^2}{4\pi r^2} e^{-r/c}
\]

and estimate its value within the limits of the dimension of the magnetic inhomogeneity. Figure 2b shows the distribution of the decrease of the magnetic moments over the coordination spheres. For the investigated alloys, the decrease of the magnetic moments of the matrix is the same within the limits of the measurement errors and extends at least over ten coordination spheres away from the impurity atom, in agreement with earlier estimates\(^{\text{[5]}} \) of the dimensions of the magnetic inhomogeneities. Thus, the magnetic inhomogeneity of the paramagnetic matrix in the investigated Invar alloys is produced by regions with decreased values of the atomic magnetic moments around clusters made up only of Fe atoms within the limits of the first coordination sphere.

3. Model of regions of magnetic polarization. With decreasing Ni concentration in the alloys, the value of \( c \) increases and the regions of the perturbation begin to overlap. Thus, at 22\% Ni, the concentration of the impurity atoms is \( c = 4\% \) and establishment of regions of long-range antiferromagnetic order of the \( \gamma \)-Fe type\(^{\text{[11-13]}} \) becomes possible in the fully perturbed matrix if the perturbing iron atoms have an appropriate magnetic moment. A direct investigation of such iron-nickel alloys at 4.2 °K is impossible, because of the martensitic transformation, but is can be assumed that at a less than 22\% nickel content regions of magnetic polarizations are produced in turn around the ferromagnetic centers even in an antiferromagnetic (or paramagnetic) matrix. Then \( dv/d\Omega \) takes the form\(^{\text{[15]}} \)

\[
\frac{dv}{d\Omega} = 0.0486c(1-c)[M_1 + M_2]^{-1}
\]

where \( C \) is the concentration of the magnetic-polarization clouds, \( M_1 \) is the 3d-moment at the center of the cloud and follows the usual 3-formfactor, and \( M_2 \) is the moment induced in the matrix with formfactor \( f(1 + x^2 S^2)^{-1} \).

A simultaneous solution of Eq. (7) and the relation \( \mu = C(M_1 + M_2) \), which is satisfied at small \( C \) in the absence of overlap of the polarization clouds, makes it possible to determine \( C \) and the average magnetic moment \( M_1 + M_2 \) per cloud.\(^{\text{[16]} \)} From the values of \( dv/d\Omega \) in Table 1 and the values of \( \mu \) from the paper of Crangle and Hallam\(^{\text{[13]}} \) we obtain for an alloy with 32\% Ni at 4.2 °K the values \( C = 7.2 \% \) and \( M_1 + M_2 = 20.8 \, \mu_B \).

Such a value of \( C \) indicates that the magnetic polarization regions overlap strongly. Therefore the nonlinear overlap effects make the foregoing analysis of the scattering only approximate for an alloy with 32\% Ni. Concentration of clusters with values of \( N \) from 7 to 12, calculated from formula (5) is 4\%. It is possible that such formations, containing 7 to 12 nickel atoms in the nearest environment of the Fe atom, are indeed the embryos of the ferromagnetism in alloys containing about 20\% Ni, as suggested by Window.\(^{\text{[17]}} \)

It appears that the magnetic-polarization clouds in Invars differ physically from the polarization clouds in Pd–Fe or Pd–Co alloys,\(^{\text{[15]}} \) and are closer in character to the clusters observed in alloys based on nickel,\(^{\text{[15,18,19]}} \) where the onset of ferromagnetism in a paramagnetic matrix is due to the composition of the cluster, that is, to the number of Ni atoms in the nearest surrounding of the Fe atom. In Invars, the ferromagnetic clouds can appear also in an antiferromagnetic matrix, and the concentration and average moment per cloud can be altered by annealing and deformation, inasmuch as atomic ordering of the Ni₂Fe type is observed in these alloys.\(^{\text{[5]}} \)

4. Long-range antiferromagnetic order. The overlap of the regions of magnetic polarization should preclude the existence of long-range antiferromagnetic order in the investigated alloys. Figure 3 shows neutron diffraction patterns of a single crystal with 35\% Ni, obtained at 4.2 and 300 °K. It is seen that within the limits of the statistical measurement error the diffraction patterns coincide for both temperatures. The statistical error of the background is decreased to 1\% in the repeated measurements. Attention is called to the absence of reflections at angles 2θ < 25° in the (100) direc-
tion. This means that the long-range antiferromagnetic order proposed by Dubinin et al. (4) does not take place in the alloy.

The neutron diffraction patterns contain the reflections \( \lambda/2 \) (200) and \( \lambda/2 \) (220), due to the presence of neutrons of wavelength \( \lambda/2 \) in the spectrum, and coinciding with the positions of the antiferromagnetic reflections of \( \gamma\text{-Fe} \). Table 2 gives the ratios of integrated intensities of the corresponding reflections as functions of the temperature without allowance for extinction. It is seen from Table 2 that the ratio of the integrated intensities remains unchanged and is equal to the contribution of the \( \lambda/2 \) component to the intensity of the incident beam. (20) Estimates of the sensitivity in the determination of the volume fractions of the antiferromagnetic phases (1-4) do not exceed 2%. (21) The results lead to the conclusion that (within the sensitivity limits indicated above) there is no long-range antiferromagnetic order in a classical Invar, a fact supported by the estimates of \( c \) in Table 1. However, if the Fe atoms at the centers of the perturbation regions have a magnetic moment oriented opposite to the moment of the surrounding atoms, (14) then a short-range antiferromagnetic order is produced, but is difficult to observe at the nonmagnetic Fe atom concentrations given in Table 1.

5. Temperature dependences. Figure 4a shows the cross sections for small-angle scattering of neutrons by an alloy with 32% Ni, measured at various temperatures. Analogous cross sections were obtained for all alloys at temperatures up to \( T/T_c = 0.95 \). A characteristic feature of the cross sections is their growth with increasing temperature. Inasmuch as the scattering surface connected with the spin-wave effects expands with increasing temperature and begins to intersect the observation angle, it is necessary to estimate the critical value \( S_\lambda \) for different temperatures. Assuming that the magnetic elasticity constant varies like \( D = D_0 (1 - T/T_c)^{1/3} \) (22) the value of \( S_\lambda \) estimated in analogy with (7) ranges from 0.04 to 0.11 \( \text{Å}^{-1} \) in the investigated temperature interval for all the alloys. The experimental points at \( S < 0.1 \text{ Å}^{-1} \) will therefore be disregarded from now on. We note that the scattering cross sections at these values of \( S \) increase more slowly than the cross sections at \( S > 0.1 \text{ Å}^{-1} \) with rising temperature, and the corresponding points fit better the straight line on Fig. 4b.

In all the temperature measurements, the dependence of \( \sigma/\partial T \) on \( T \) is described by the Lorentzian (3), and the solid curves in Fig. 4a were calculated from the values of \( (\sigma/\partial T)_0 \) and \( \times \) from Fig. 4b. The temperature-induced changes in the values of \( \times \) and \( (\sigma/\partial T)_1/2 \), where \( \sigma_T \) and \( \sigma_0 \) are the cross sections at \( S = 0 \) for \( T \text{ K} \) and \( 0 \text{ K} \), respectively, are shown in Figs. 5 and 6.

It is seen from Fig. 5 that the theoretically predicted(10) relation \( \times = B(T_c - T)^{1/3} \) holds for all the alloys. If it is assumed that this relation holds also for \( T > T_c \), then the temperatures at which \( \times = 0 \) vary linearly from 730 to 790 K when the Ni concentration changes respectively from 40 to 32%. In turn, if a

| Table 2. |
|---|---|---|
| \( T, \text{K} \) | \( \lambda/2 \) (200) | \( \lambda/2 \) (220) |
| 4.2 | 0.19±0.01 | 0.17±0.01 |
| 3.0 | 0.21±0.01 | 0.17±0.01 |

FIG. 3. Neutron diffraction patterns of a single crystal with 35% Ni. Directions: a- <001>, b-<110>; c-1.2°K, x-300°K.

FIG. 4. a) Cross sections of small-angle magnetic scattering of neutrons by alloy with 32% Ni: 1 - 4.2 K, 2 - 77 K, 3 - 90 K, 4 - 293 K; b) dependence of \( (\sigma/\partial T)^{1/2} \) on \( S^2 \).

FIG. 5. Temperature dependences of \( \times \). ⊗ - 46% Ni, ◦ - 38% Ni, ▲ - 36% Ni, ▲ - 35% Ni, ● - 34% Ni, ○ - 32% Ni.
similar dependence of $\kappa$ is assumed for alloys with $y<32\%$, then linear extrapolation of the data from Fig. 2a to the values at $\kappa=0$ yields $y=26\%$, that is, a quantity close to nickel content in alloys in which presumably ferromagnetism sets in at $T=0$ K in the $\gamma$ phase of the Fe-Ni system.

The temperature dependence of $\frac{d\sigma}{dT}$ reflects the change of the dynamic magnetic inhomogeneities in the ferromagnetic system. Starting from the model of magnetic inhomogeneity described above, the investigated alloys can be regarded as systems with magnetic atoms in a ferromagnetic matrix. The influence of the nonmagnetic impurity was investigated by Lovesey and Marshall,\(^{16,23}\) using the Heisenberg model in the molecular-field approximation. The experimental results given in Fig. 6 agree well with the calculated temperature dependences.\(^{106}\) The growth of the cross sections with increasing temperature is due to the increase of the range of influence of the impurity on the magnetization in the alloy, thereby enhancing the dynamic inhomogeneity of the ferromagnet.

The temperature dependences in Fig. 6 show that the larger the statistical inhomogeneities in the alloy, the lower the temperatures at which the growth of the number of dynamic inhomogeneities begins. The "law of corresponding states" is therefore not satisfied in Invar alloys.\(^{12}\) In addition, the temperature dependences for alloys with 32–35\% Ni, shown in Fig. 6, agree better with the curves calculated with allowance for antiferromagnetic pairing of the magnetic moments of the matrix atoms in indirect exchange of the interaction via the impurity.\(^{22}\) Thus, the model of the magnetic inhomogeneity does not exclude the possibility of the presence, in Invar alloys, of short-range antiferromagnetic order of pure exchange origin, proposed by Kondorskiy and Sedov.\(^{24}\)

It follows also from Fig. 6 that at $T/T_C>0.8$ the quantity $M/M_0$, where $M_0$ corresponds to $T=0$ K, approaches a singularity like $(T_C-T)^{\nu}$ with values of $\nu$ from 0.3 to 0.5 when the Ni concentration changes respectively from 32 to 40\%. The deviation from the predicted value $\nu=1$.\(^{106}\) is apparently due to the already mentioned singularities in the temperature dependence of the saturation magnetization of Invar alloys.

3. CONCLUSION

As a result of a study of magnetic diffuse scattering of neutrons in Invars, static magnetic inhomogeneities were observed at $T=0$ K. The scattering cross section is satisfactorily described with the aid of a model of regions with decreased values of the magnetic moments around the nonmagnetic atoms in the ferromagnetic matrix or a model of regions of magnetic polarization. Both models exclude the coexistence of long-range ferromagnetic and antiferromagnetic orders in the investigated alloys, but admit of the onset of short-range antiferromagnetic order in the ferromagnetic matrix. Neutron diffraction at 4.2 K has confirmed the absence of long-range antiferromagnetic order in classical Invars. The temperature dependences of the scattering cross-sections agree well with the description of neutron scattering by a ferromagnetic system with nonmagnetic impurity, in which a dynamic magnetic inhomogeneity is produced. For alloys with 32–35\% Ni, the temperature dependence of the cross sections admit of the onset of short-range antiferromagnetic order as a result of indirect exchange interaction via a nonmagnetic impurity.

\(^{17}\) V. I. Goman’kov, Pis’ma Zh. Eksp. Teor. Fiz. 21, 590 (1975) [JETP Lett. 21, 276 (1975)].

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