Critical scattering of neutrons in Invar iron-nickel alloys

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(Submitted May 22, 1975)
Zh. Eksp. Teor. Fiz. 70, 163–171 (January 1976)

A study was made of small-angle neutron scattering in iron-nickel alloys with 50, 60, 63, 65, 68, and 70 at.% Fe. The measurements were carried out in a wide temperature range of 80–1000°K. The elastic and inelastic contributions to the scattering were separated by a magnetic field applied at right-angles and parallel to the scattering vector. The temperature range of critical scattering increased with iron content. The theory of critical scattering of neutrons was used to calculate dimensions of regions of longitudinal and transverse spin correlation which were similar (9–12 Å) for the Invar alloys and depended weakly on temperature. The temperature dependences of the longitudinal and transverse components of the magnetic susceptibility tensor were determined. The anomalous critical scattering in Invar alloys was found to be associated with a spatially inhomogeneous magnetic structure resulting from the existence of a mixed exchange interaction between atoms.

PACS numbers: 75.25.+z

Magnetic critical scattering of neutrons, due to the appearance of spontaneous magnetization fluctuations near the Curie point, has been investigated thoroughly in iron,[1–3] nickel,[4–6] and cobalt.[7] The most careful measurements were carried out on nickel using polarized neutrons.[6] Critical scattering has been investigated less thoroughly for alloys. However, according to the available data,[8] random fluctuations of atoms in the immediate environment of a selected site result in the "smearing" of the second-order phase transition along the temperature scale so that the critical scattering range is wider than in the case of pure metals. This effect is even more important in alloys with a mixed exchange interaction. In this case, the critical scattering may be observed at temperatures well below the Curie point because of the existence of magnetization fluctuations resulting from the antiferromagnetic interaction between individual atoms in an alloy.

A classical example is the system of iron–nickel alloys for which different signs of the exchange integrals ($J_{NiNi}>0$, $J_{FeNi}>0$, and $J_{FeFe}<0$) have been demonstrated experimentally.[9,10] The small-angle scattering of neutrons in these alloys was investigated for the first time at low temperatures (100 °K) in[11,12] and it was concluded that a spatially inhomogeneous magnetic structure is present in the ground state of Invar alloys. The influence of temperature was estimated by measuring the small-angle scattering at 293 and 393 °K.[13] Similar effects were then also observed by other authors.[14–16] However, the critical scattering of neutrons near the Curie point was investigated only in[17] in a crystal of just one alloy 65Fe–35Ni.

The absence of a full and systematic study of the critical scattering in iron–nickel alloys in a wide range of compositions and temperatures has been an obstacle in gaining a clear understanding of the role of the antiferromagnetic and temperature contributions to the total small-angle neutron scattering. Our aim to fill this gap by a careful study of small-angle scattering in iron–nickel alloys in the Invar region near the Curie temperature and well below it. An important feature of our investigation was the separation of the elastic and inelastic neutron scattering by applying magnetic fields of suitable direction relative to the scattering vector.

EXPERIMENTAL METHOD

The small-angle neutron scattering was investigated in iron–nickel alloys mainly in the range of compositions in which the average magnetic moment deviated from the mixing law. Alloys with 50, 60, 63, 65, 68, and 70 at.% Fe in nickel were prepared by vacuum fusion from pure components. After prolonged homogenization (~ 100 h) at 1100 °C, the samples were quenched in water so as to obtain the most disordered state. According to x-ray structure analysis, all the alloys had the fcc lattice right down to liquid nitrogen temperature. Only the alloys with 68 and 70 at.% Fe exhibited a martensitic transition below room temperature.

The small-angle scattering effects were measured with a diffractometer placed in a horizontal channel of the IVV-2 reactor, where a monochromatic neutron beam of 1.13 Å wavelength was formed. We studied the scattering of neutrons transmitted by 20×20 mm samples, 2 mm thick. A collimator placed in front of a sample made it possible to record the minimum scattering angle of $2\theta = 1°\ 10'$. The minimum angle in the determination of the angular dependences was $2\theta = 5°$. This range of angles corresponded to 0.1–0.5 when expressed in terms of $K = 4\pi\lambda^{-1}\sin\theta$. The influence of temperature was investigated in the range from 80 to 1000 °K. The Curie point of the alloys was found to be located between 300 and 800 °K. Very careful measurements of the temperature dependence of the cross section were made for the angle $2\theta = 1°\ 10'$.

A sample was placed in a specially built cryostat. Temperatures below the room value were obtained using liquid nitrogen and a heater, which stabilized the temperature of a sample to within 1 °C. The temperature was monitored by two copper–constantan thermocouples bonded to the upper and lower parts of the sample. Before each measurement, the temperature gradient in the sample was reduced to a minimum. The critical scat-

tering was observed in the absence of a magnetic field and in a field applied at right-angles and parallel to the scattering vector. The different directions of the field were produced in a ring electromagnet ($H \approx 10$ kOe). The use of this electromagnet extended considerably the range of potential measurements and made it possible to study the critical scattering in alloys magnetized in different ways relative to the scattering vector.

The differences between the factors influencing the background in two positions of the magnet were eliminated by making four measurements of the intensity for each angle: $I_0^{\parallel}$, $I_H^{\parallel}$ and $I_0^{\perp}$, $I_H^{\perp}$, from which the differences $I_{0-\parallel}$ and $I_{0-\perp}$ were calculated.

All the measured intensities were reduced to cross sections by a vanadium scatterer. The final values of $d\sigma/d\Omega$ were corrected for multiple and double magnetic scattering of neutrons, in accordance with[18]. All the numerical calculations were carried out on a computer. It was found that, for the thicknesses of the samples used in our study, these corrections were small.

EXPERIMENTAL RESULTS

The general qualitative pattern of the critical scattering at the angle $2\theta = 1°10'$ in the absence of a magnetic field is shown in Fig. 1 together with the data for nickel taken from[4]. We can see that the critical scattering in alloys extends over a wider range of temperatures than in pure nickel. As the iron concentration is increased, this range expands. For example, in the case of the 50Fe alloy, located in the linear part of the concentration dependence of the average magnetic moment per atom $\mu(c)$, the critical scattering begins from about $0.7T/T_c$, whereas, in the Invar alloy 65Fe–35Ni, which exhibits a considerable deviation of $\bar{\mu}$ from the mixing law, it exists throughout the investigated temperature range.

Very similar temperature dependences also apply to the scattering cross sections $(d\sigma/d\Omega)_{\parallel}$ and $(d\sigma/d\Omega)_{\perp}$. However, there are some features which are revealed most clearly by the difference curves $(d\sigma/d\Omega)_{0-\parallel}$ and $(d\sigma/d\Omega)_{0-\perp}$, plotted in Fig. 2. We can see that $(d\sigma/d\Omega)_{0-\parallel}$ has a peak near the Curie point and $(d\sigma/d\Omega)_{0-\perp}$ has an additional wide maximum whose position shifts toward lower temperatures with increasing iron concentration. This is exhibited more clearly by $(d\sigma/d\Omega)_{\parallel-\perp}$ in the third column in Fig. 2.

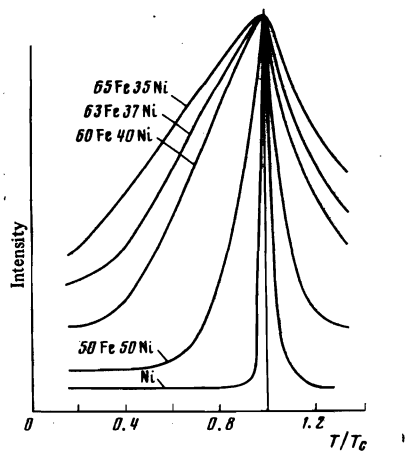

FIG. 1. Qualitative comparison of the temperature dependences of the critical scattering at the angle $2\theta = 1°10'$ ($H = 0$). The curve for Ni is taken from[4].

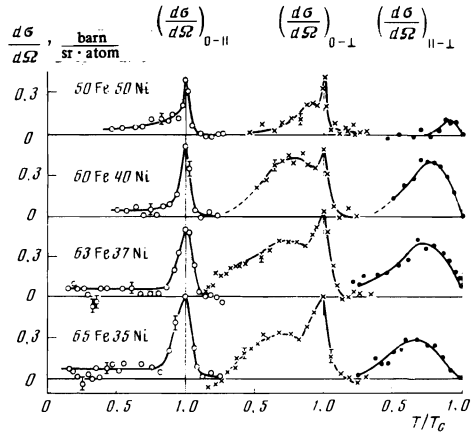

FIG. 2. Temperature dependences of the difference scattering cross sections obtained for various alloys at the angle $2\theta = 1°10'$.

The angular dependences of the room-temperature difference cross sections are plotted in Fig. 3. An increase in the iron concentration results in characteristic angular dependences of $(d\sigma/d\Omega)_{0-\parallel}$ and $(d\sigma/d\Omega)_{0-\perp}$. The former shows a smooth increase with decreasing scattering angle, whereas the latter has negative values for large angles, passes through zero, and rises steeply at small angles. The influence of temperature on the angular dependences of the difference cross sections is demonstrated in Fig. 4 for the 65Fe–35Ni Invar alloy. We can see that, on approach to the Curie point ($T_c = 500°$ K), the gap between the curves decreases considerably and in the paramagnetic region the curves are almost identical. Moreover, there is a general tendency for the scattering cross sections to increase on approach to the Curie point and the values of $d\sigma/d\Omega$ are almost identical at the Curie point and in the immediate vicinity of this point because the mag-

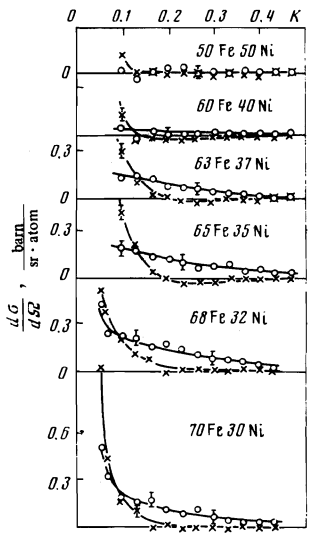

FIG. 3. Angular dependences of the difference cross sections obtained at room temperature for various alloys ($K = 2\pi\lambda^{-1}\sin\theta$): ○) $(d\sigma/d\Omega)_{0-\parallel}$; ×) $(d\sigma/d\Omega)_{0-\perp}$.

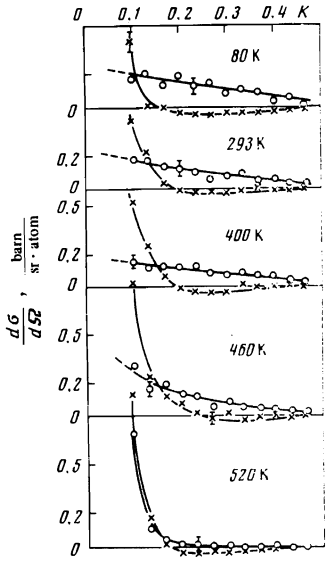

FIG. 4. Angular dependences of the difference cross sections obtained at various temperatures for the 65Fe–35Ni alloy ($K = 2\pi\lambda^{-1}\sin\theta$): ○) $(d\sigma/d\Omega)_{0-\parallel}$; ×) $(d\sigma/d\Omega)_{0-\perp}$.

netic system becomes insensitive to the direction of the magnetic field relative to the scattering vector.

A characteristic steep rise exhibited in the small-angle range by $(d\sigma/d\Omega)_{0-\perp}$ and a wide maximum in the temperature dependence of this cross section are due to the inelastic scattering of neutrons by spin waves. In fact, experiments reported in[9,10] establish that the limiting angles for the inelastic scattering θ_0 at 0°K and $H = 0$ are 29, 37, 41, and 45', respectively, for the alloys with 50, 60, 63, and 65 at.% Fe. If we bear in mind that these angles increase with temperature and field, the maximum of $(d\sigma/d\Omega)_{\parallel-\perp}$ can be reliably identified with the temperature range of the existence of spin waves in iron–nickel alloys. It is clear from Fig. 3 that, in the case of the 50Fe alloy, the spin waves exist right up to the Curie point, whereas, in alloys of Invar composition, characterized by considerable magnetic inhomogeneities, these waves exist only up to $T/T_c \approx 0.7-0.8$.

Thus, the inelastic scattering of neutrons is manifested largely by the angular dependences of $(d\sigma/d\Omega)_{0-\perp}$ and this is observed in a fairly narrow range of angles (up to $K = 0.1-0.15$). The difference cross section $(d\sigma/d\Omega)_{0-\parallel}$ behaves quite differently. Its angular dependences are free of the inelastic contributions right up to small values of K. Therefore, this cross section can be used in the calculation of the transverse and longitudinal components of the magnetic susceptibility tensor of the investigated alloys.

DISCUSSION OF RESULTS

The thermodynamic theory of the critical scattering of neutrons was developed by Krivoglaz.[19] According to this theory, the differential cross section for the scattering of unpolarized neutrons in cubic crystals in an arbitrary magnetic field is

$$\frac{d\sigma}{d\Omega} = CV|f_n|^2 kT\left[\frac{1+e_z^2}{\chi_\perp^{-1}+\alpha q_n^2}+\frac{1-e_z^2}{\chi_\parallel^{-1}+\alpha q_n^2}\right], \tag{1}$$

where C is a constant, V is the volume, f_n is the magnetic form factor, and e_z is the cosine of the angle between the scattering vector and the magnetic field. The longitudinal and transverse components of the magnetic susceptibility tensor $\chi_\parallel$ and $\chi_\perp$ are, by definition (for $\alpha q_n = 0$), related in the following way to the parameters r_1 and k_1 of the Van Hove[20] and de Gennes[21] theories:

$$\chi_\parallel = 1/(k_\parallel r_1)^2,\ \chi_\perp = 1/(k_\perp r_1)^2, \tag{2}$$

where

$$r_1 = \frac{a^2}{Z}\frac{T_c}{T}, \tag{3}$$

a is the lattice parameter, Z is the number of nearest neighbors, and k_1^{-1} represents the macroscopic size of critical fluctuations.

The formula (1) describes the behavior of an ideal ferromagnet near the Curie temperature but is also valid well below the Curie point if magnetization fluctuations exist for some reason in a magnetic system. This situation occurs in alloys[19,22] and then the longitudinal component of the magnetic susceptibility tensor in Eq. (3) becomes dependent on the longitudinal magnetization for certain concentrations and in the low-temperature limit it assumes the form of the Marshall formula[23] for the cross section of diffuse scattering of neutrons by spatially inhomogeneous magnetic structures:

$$\frac{d\sigma}{d\Omega} = CV|f_n|^2(1-e_z^2)c(1-c)\left(\frac{\partial M}{\partial c}\right)^2. \tag{4}$$

This type of scattering was investigated by us in[11,12].

We must consider specially the nature of the small-angle neutron scattering. The dynamic nature of magnetic fluctuations makes the scattering inelastic. However, since the interaction time of a neutron with magnetization fluctuations is still shorter than the relaxation time of the fluctuations, the scattering is elastic and only at the Curie point can we regard it as quasi-elastic. Therefore, all the above formulas apply to the elastic part of the small-angle scattering. However, since, at small angles, there is inelastic scattering of neutrons by spin waves, which is limited to a certain limiting angle (up to ~1°), in which case the difference cross section $(d\sigma/d\Omega)_{\parallel-\perp}$ is positive, allowance for such scattering becomes extremely important in studies of the critical process.

The expression (1) simplifies if a specific direction of the magnetic field relative to the scattering vector is selected. If $T < T_c$ and $\alpha q_n = 0$, we have

$$\left.\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_\parallel &= 2CVkT\chi_\perp, \text{ for } \mathbf{H}\parallel\mathbf{e},\\ \left(\frac{d\sigma}{d\Omega}\right)_\perp &= CVkT(\chi_\perp+\chi_\parallel), \text{ for } \mathbf{H}\perp\mathbf{e}.\end{aligned}\right\} \tag{5}$$

In the absence of a field ($H = 0$), we obtain

$$\left.\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_0 &= \frac{2}{3}CVkT(2\chi_\perp+\chi_\parallel) \text{ for } T<T_c,\\ \left(\frac{d\sigma}{d\Omega}\right)_0 &= 2CVkT\chi, \text{ где } \chi_\perp=\chi_\parallel=\chi \text{ for } T\geqslant T_c.\end{aligned}\right\} \tag{6}$$

It is usual to determine experimentally the difference between the scattering patterns of nonmagnetized and magnetized samples.

We then obtain from Eqs. (5) and (6):

$$\left.\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_{0-\parallel}&=\frac{2}{3}CVkT(\chi_\parallel-\chi_\perp),\\ \left(\frac{d\sigma}{d\Omega}\right)_{0-\perp}&=-\frac{1}{3}CVkT(\chi_\parallel-\chi_\perp),\\ \left(\frac{d\sigma}{d\Omega}\right)_{\perp-\parallel}&=CVkT(\chi_\parallel-\chi_\perp).\end{aligned}\right\}\qquad(7)$$

It follows from the relationships (7) that the elastic scattering cross sections $(d\sigma/d\Omega)_{0-\parallel}$ and $(d\sigma/d\Omega)_{0-\perp}$ have opposite signs and differ by a factor of two in magnitude. It is clear from Figs. 3 and 4 that these conditions are satisfied well at large angles and the inelastic contributions to $(d\sigma/d\Omega)_{0-\perp}$ spoil this pattern only for $K = 0.1-0.15$.

Measurements of the absolute cross sections for various relative orientations of the field and the scattering vector give information on the longitudinal and transverse components of the magnetic susceptibility tensor, i. e., on the longitudinal and transverse correlations of the total magnetic moment. The susceptibilities calculated in this way for some alloys are plotted in Fig. 5. We see that both $\chi_\parallel$ and $\chi_\perp$ rise in the same way with temperature but, near the Curie point, there is a considerable difference between them. In particular, the amplitude of the maximum of $\chi_\parallel$ is higher and it is narrower than that of $\chi_\perp$. Moreover, when the iron concentration is increased, the maximum of $\chi_\perp$ does not coincide with the Curie point but shifts to lower temperatures.

Equations (2) and (3) and the susceptibility data can be used to calculate the dimensions of transverse and longitudinal spin correlations. These are shown in Figs. 6 and 7 for the investigated alloys in comparison with one another and with the results reported for pure nickel and iron in[5]. It is clear from Fig. 6 that there is a considerable difference between the dimensions of magnetic fluctuations near the Curie point for Fe and Ni and their alloys. Only the 50Fe–50Ni is closest in this respect to pure metals. The behavior of the dimensions of longitudinal and transverse spin correlations is compared in Fig. 7. It is characteristic that an increase in the iron concentration in the alloy results in practically the same increase in $k_\parallel^{-1}$ and $k_\perp^{-1}$ and, in the case of the Invar alloy 65Fe–35Ni, the dimensions remain almost constant throughout the investigated temperature range and amount to 9–10 Å. If the calculations are made using the cross sections found by extrapolation to zero scattering angle, the values of $k_{\parallel,\perp}^{-1}$ increase to 11–12 Å, which are only slightly different from the values obtained for the angle $2\theta = 1°10'$. It is interesting to note that the radius of inertia of such inhomogeneities is calculated in[15] and found to be $R \approx 9$ Å. In our opinion, these values are in good agreement with one another.

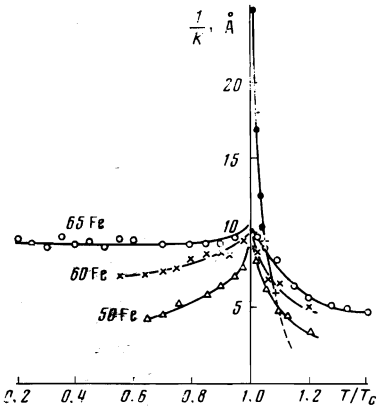

FIG. 6. Temperature dependences of the dimensions of the longitudinal spin correlation in iron (●), nickel (+),[5] and Fe–Ni alloys.

Another important feature of the $k_\parallel^{-1}$ and $k_\perp^{-1}$ curves is their different behavior in the region of the Curie point: $k_\parallel^{-1}$ has a definite peak, whereas $k_\perp^{-1}$ decreases ahead of the Curie point. The latter behavior is clearly due to the disappearance of spin waves on approach of the alloy to the Curie point.

The weak temperature dependence of the dimensions of longitudinal and transverse spin correlations in Invar alloys is evidently due to the presence of a spatially inhomogeneous magnetic structure, characterized by magnetization fluctuations in the ground state, due to the mixed nature of the exchange interaction in these alloys. Bearing this point in mind, we can regard the magnetic structure of Invar alloys as collinear ferromagnetic with magnetization fluctuations or magnetic inhomogeneities extending over three or four coordination spheres. The most probable centers of deviation

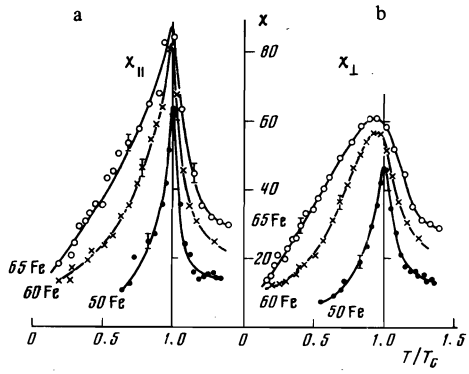

FIG. 5. Temperature dependences of the longitudinal $\chi_\parallel$ and transverse $\chi_\perp$ components of the magnetic susceptibility tensor of iron–nickel alloys.

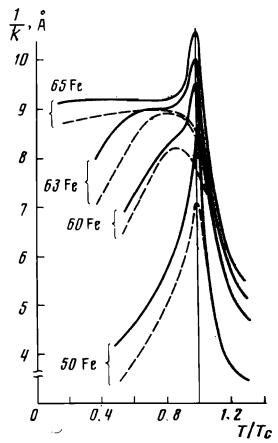

FIG. 7. Comparison of the temperature dependences of the dimensions of longitudinal and transverse spin correlations in Fe–Ni alloys. The continuous curves represent $k_\parallel^{-1}$ and the dashed curves $k_\perp^{-1}$.

of the magnetic moment of atoms from the spontaneous magnetization direction are random fluctuations of iron atoms whose immediate environment has twelve atoms of the same kind, in accordance with the ideas put forward in[24,12]. It is interesting to note that, when the dimensions of these fluctuations remain constant, the demagnetization—which increases with temperature—clearly occurs due to the accumulation of such fluctuations by the capture of new iron atoms acting as fluctuation centers with the immediate environment of less than 12 iron atoms.

Thus, a mixed exchange interaction in alloys is manifested by the characteristic features of the critical scattering of neutrons near the second-order phase transition temperature, which should be regarded as a wide temperature range where an inhomogeneous magnetic structure loses almost completely its spin order. The additional influence of the antiferromagnetic interaction on the demagnetization of the system results, in particular, in the anomalous temperature dependence of the linear expansion coefficient of Invar alloys.

The authors are grateful to Yu. A. Dorofeev and A. E. Teplykh for their help in the experiments.

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Translated by A. Tybulewicz