Temperature dependence of spin fluctuation scattering of neutrons on pyrrhotite
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TEMPERATURE DEPENDENCE OF SPIN FLUCTUATION SCATTERING OF NEUTRONS ON PYRRHOTITE (1)

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Résumé. — A l'aide du spectromètre à neutrons triple axe de Cracovie installé à Vinca (Yougoslavie), la diffusion cohérente inélastique des neutrons de longueur d'onde $\lambda = 1.376$ Å liée au point $\tau = (001)$ a été étudiée à différentes températures jusqu'à $400 \, ^\circ C$, c'est-à-dire, bien au-dessus de la température critique ($T_N = 320 \, ^\circ C$).

L'intensité du cône de diffusion $(001)$, augmente avec la température, mais son caractère « magnon » reste sans changement. Néanmoins, à partir de $200 \, ^\circ C$, les raies « magnons » commencent à s'élargir. Cette température n'est pas très sensible à l'énergie d'un groupe de magnons donnés. Le degré élevé d'inélasticité se maintient au-dessus de la température critique, et le transfert moyen d'énergie reste très voisin de celui à basse température. Les résultats sont discutés en fonction de la durée de vie des magnons et de l'effet de la température sur le couplage d'échange effectif.

Abstract. — By means of the triple axis Cracow neutron spectrometer installed at Vinca (Yugoslavia), coherent inelastic scattering of monochromatic neutrons ($\lambda = 1.376$ Å) connected with $\tau = (001)$ was investigated at various temperatures above room temperature up to $400 \, ^\circ C$, i.e. above the critical point ($T_N = 320 \, ^\circ C$) of the spin alignment in pyrrhotite. The intensity of the $(001)$ scattering cone increases with temperature but its magnon character does not change. Only at temperatures above $200 \, ^\circ C$ do the widths of the magnon peaks begin to increase. This temperature is not very sensitive to the energy of a given magnon group. The high degree of inelasticity is maintained over the critical point region and the mean energy transfer is close to the one for low temperatures. The results are discussed in terms of magnon lifetime and temperature dependence of effective exchange coupling.

I. Introduction. — While the magnetic inelastic scattering of neutrons sufficiently below the critical point of spin alignment in crystals is well described by existing theories, this cannot be said with certainty of the situation arising in the vicinity of the critical point.

For lower temperatures the scattering can be analysed applying directly spin wave theory as mentioned in [15]. At temperatures near the critical point the spin wave approximation loses its validity and the more general formalism, invented by Van Hove [14], has to be introduced, describing the system by time dependent spin correlation functions. Neutron scattering cross-sections are their integral transforms. Thus the problem was reduced to finding the expressions for spin correlation functions. At low temperature they can be related with spin wave theory and give the same picture [3], [14]. In the critical region their behaviour is represented in terms of $r_1$, $x_1$, $\Lambda_1$ parameters introduced by Van Hove [14] and discussed by others authors [2], [3], [9] as well as measured in a number of neutron scattering experiments [6], [10], [13].

Crucial in the problem is the inelasticity of scat-
tering connected with the magnitude of the spin diffusion constant $\Lambda_1$. It was believed that $\Lambda_1$ is zero at the critical point making the scattering elastic. However, recent neutron investigations [6], [11] do not seem to corroborate this opinion. Hence it was interesting to extend the measurements described in [15] to the region of higher temperatures.

II. Measurements. — Measurements were performed in Vinca by a technique essentially the same as that described in [15], using the Cracow Neutron Spectrometer and the same crystal of pyrrhotine. For this reason the description of many details which can be found in [15] will not be repeated.

The crystal sample was placed in a furnace (see fig. 1) mounted not on the goniometer head but on a special plate with an adjustable position. This plate could be fixed on the axis of any spectrometer table, and the position of the furnace properly adjusted. The temperature inside the furnace was measured by a device controlling the voltage applied to the heating wire.

The measurements of the magnetic scattering were carried out both by the diffraction and the energy analysing techniques using the same wave length ($\lambda_0 = 1.376$ A) of incident neutrons.

The angular distribution of intensity within the cone of scattered neutrons connected with $\tau = (00.1.)$ was investigated at a number of different temperatures for five missetting angles $7.5^\circ$, $15^\circ$, $23^\circ$, $33^\circ$, and $41^\circ$. Some of the obtained curves are represented in figures 2 and 3.

![Fig. 2](image_url1)

**Fig. 2.** — Family of diffraction curves for $\Delta \theta = 15^\circ$ and for different temperatures. Background was subtracted and curves drawn aside in the vertical direction with unit of the scale constant: $\varphi_c =$ theoretical position of the centre of the peaks.

![Fig. 3](image_url2)

**Fig. 3.** — Family of diffraction curves for $\Delta \theta = 41^\circ$ and for different temperatures.

For the energy analysis two methods of observations were used. At first for $\Delta \theta = 23^\circ$ the conventional way of analysing was applied but without collimation in the vertical plane usually applied between the sample (placed on table II) and the analyser (Zn-crystal placed on table I). At this missetting angle the instrumental reso-
solution was sufficient for the separation of intensities from the magnon and elastic scattering at room temperature. Thus the situation in reciprocal space discussed in [10] (see fig. 2 of [10]) could be studied. The curves obtained in this way can be seen in figure 4.

They directly show that the diffuse peaks observed by diffraction technique should be entirely ascribed to inelastic scattering in the whole temperature range.

In order to check this inference for other energies (missetting angles) another method was used, i.e. the intensity of scattered neutrons was recorded at constant energy and momentum transfer, by setting the analyser (Zn-crystal and detector) in a predetermined fixed position. This position was chosen in such a way that the detecting spot in reciprocal space (in laboratory frame) was centered around the point which corresponded to the end of the $\tau$-vector when the crystal sample was misaligned by a given angle $\Delta \Theta_c$.

The number $N$ of detected neutrons was then recorded for different positions $\Delta \Theta$ of the sample when it was rotated in steps around the vertical axis. For $\Delta \Theta$ close to $\Delta \Theta_c$ the corresponding fragment of the scattering surface entered the detecting spot and the counting rate increased. On theoretical grounds the spectra should exhibit left and right symmetry around $\Delta \Theta_c$, which was roughly observed (therefore curves on figure 5 are symmetrised).

An important advantage of the method is the constancy of the analysing system efficiency. This is not fulfilled when the detecting spot is caused to wander because of the Renninger effect in the analysing crystal. $(\Delta \Theta - \Delta \Theta_c)$ directly gives the $q$-value because $q = \tau |\Delta \Theta - \Delta \Theta_c|$ for not too high $(\Delta \Theta - \Delta \Theta_c)$.

The measurements were performed at various temperatures of the sample for two different energy transfers $\Delta E$ equal 13 meV and 16.5 meV which correspond to $\Delta \Theta_c$ equal 41° and 59° respectively. The vertical collimation used was respectively 1°.

**Fig. 4.** Family of curves obtained by the conventional energy analysing method at various temperatures ($T_N = 320 \degree C$) for $\Delta \Theta = 23^\circ$ ($E_{\text{spin wave}} = 8.1 \text{ meV}$) without additional collimation in the vertical plane:

- $\lambda_0$: theoretical position of the centre of the elastic peak.
- $\lambda_\epsilon$: theoretical position of the centre of the inelastic peak.

**Fig. 5.** Family of curves obtained by the constant energy transfer method at various temperatures for the position of the analysing spot lying around the end of the vector $\tau$ for $\Delta \Theta_c = 59^\circ$ — subtraction of the background and symmetrisation procedures were applied.
III. Analysis of the results. — The results were analysed under the assumption of the existence of collective motion excitations in the whole investigated region of temperatures, which at lower temperatures were identified with magnons. This point of view has recently obtained some theoretical [7], [8] as well as experimental [11] support. However, it should be noted that the experiments could not distinguish contributions from transverse and longitudinal spin fluctuations [10]. Thus it had to be assumed for the purpose of practical elaboration of the results that the excitations are of a single type and possess a certain dispersion relation $\hbar \omega(q)$ (defined for the centre of $\omega_q$-distribution) together with an energy width $\gamma$ of the "magnon" lines [5], [11]. Then the observed diffuse scattering peaks in an energy interval $\Delta(h \omega)$ should depend on two parameters: effective exchange energy (if the form of the dispersion curve is conserved) and energy width $\gamma$. Approximate calculations, explained in the appendix, made it possible to obtain the temperature dependence and to estimate the numerical values of these parameters. The energy width can be related to the excitation life time $\tau = \hbar/\gamma$.

They are confronted in figure 6. But because the applied instrumental curve (Bragg peak profile) is only an approximation, the lower temperature values of $\Delta \Gamma$ can be taken as representing the real instrumental width, although depending on missetting angle. Life times derived under this assumption are presented in figure 7. Figure 8 and 9 show respectively temperature dependences of $\Gamma_{1/2}$ and effective exchange energies $\tilde{I}$, derived from them (maintaining the form of the dispersion law [15]).

The curves obtained by the constant energy transfer method (fig. 5) are not very suitable for elaboration because of low instrumental resolution and existence of the central peak (it was ascribed [15] to the optical mode and as can be inferred from figure 5 the character of the temperature dependence of this mode is more rapid then for the acoustic one). In order to obtain information about the magnon life times the analysis of slopes was preferred so as to avoid the influence of the central maxima (the presence of which disturbed for large $\Delta \theta$ the picture of the acoustic ones). The slope of the curve obtained at room temperature was taken as corresponding to excitations with infinite life times. The changes in slope could then be considered as caused by line broad-
Fig. 8. — The temperature dependence of the $T_{\text{th}}$ widths for different missettings. Curves normalized to unity at room temperature. Curves denoted by R I and R II are obtained from curves represented in reference [11] by reduction of the temperatures by a factor 

$$\left( \frac{T_\text{FeS}}{T_\text{FeS}} \right) \frac{1}{T_\text{FeS}}.$$

denoting. When the $q$ (wave vector) distribution at
constant $\omega$ was taken as gaussian, the diminution
of the slope could easily be connected with $\gamma$.
The values of life times deduced in this way from
these curves (for $\Delta \theta_e = 41^\circ$) are presented in
figure 7.

One of the curves for $\Delta \theta_e = 59^\circ$, above the
critical point, was compared with the theoretical
distribution given by the Van Hove's [14] formula,
reduced to the form:

$$\frac{dN}{dq d\omega} \sim \text{const.} \frac{\Lambda_1(2\pi q)^2}{\omega^2 + (2\pi q)^2 + \Lambda_1^2(2\pi q)^4} \quad (1)$$

where weak terms have been neglected.

As can be seen from fig. 10, the character of the
peak is more or less satisfactorily reproduced.
Unfortunately the correction for resolution cannot
be performed with reliable accuracy. However,
the distortion of the form of the wings should not
be so serious as in the central part of the distrib-
ution. The comparison of the curves in figure 10
leads to the estimate: $\Lambda_1 = (40 \pm 10) \times 10^{-3}$
c. g. s. units and $x_1 \leq 1 \times 10^{-2}$ Å⁻¹.

In order to find how the temperature changes
the intensity of a different excitation group, the
areas under the diffuse peaks (see for instance

Fig. 9. — The temperature dependence of the exchange
stiffness $I_1$. Points for different missettings were
calculated under the assumption of the validity of the
dispersion law — see reference [15]. Values of $T_{\text{th}}$ were
taken from curves represented in figure 8. At room
temperature all points are normalized to $I_1 = 1.1$ meV.
The solid line shows the changes of square root of the
relative intensity of Bragg reflection.

Fig. 10. — The comparison of the observed peak
($T = 340$ °C — see fig. 5) profile with the profiles given
by formula (1) for different $x_1$ and $\Lambda_1$:

1. $x_1 = 1.2 \times 10^{-2}$ Å⁻¹, $\Lambda_1 = 6.8 \times 10^{-2}$ cm²/s
2. $x_1 = 0.6 \times 10^{-2}$ Å⁻¹, $\Lambda_1 = 3.4 \times 10^{-2}$ cm²/s
3. $x_1 = 1.2 \times 10^{-2}$ Å⁻¹, $\Lambda_1 = 3.4 \times 10^{-2}$ cm²/s
4. $x_1 = 0.6 \times 10^{-1}$ Å⁻¹, $\Lambda_1 = 3.4 \times 10^{-2}$ cm²/s
5. The curve 4 modified by roughly estimated instru-
mental resolution.
fig. 2) were integrated. These are presented in figure 11. The theoretical curve seen in the same figure was calculated from the approximate formula:

$$\frac{J_1}{J_0} \sim \frac{\sinh kT - 1}{\cosh kT - 1} \theta(kT) (\frac{\Gamma_2}{\Gamma_0})^2$$  \hspace{1cm} (2)

(taking into account the observed temperature variation of \(\Gamma_{1/2\hbar}\) (see fig. 8) and the Bose-Einstein population factor.

There are also marked points obtained for \(\Delta \theta = 23^\circ\) (see fig. 4) by the energy analysing technique. Of course they cannot give the same dependence as that observed by the diffraction technique because of the peak widening. However, the discrepancy has the expected sign.

IV. Discussion of the results. — The qualitative behaviour of the scattering when the temperature changes appears to be identical as in other magnets — Fe\(_3\)O\(_4\) [12], Fe\(_2\)O\(_3\) [13], Fe [6] so far investigated. For a general discussion of the effects the reader is referred to [10]. Because of the lack of any firm theoretical basis which could be applied to the case under investigation, the discussion must be limited to a comparison with the results obtained for Fe\(_3\)O\(_4\), for which the largest amount of data has been assembled by other experimental works [1], [12], [11].

It is interesting to note that in pyrrhotite the life times of excitations are about an order of magnitude smaller than in Fe\(_3\)O\(_4\). These are the only two substances where they have been estimated.

The point in which the parameters of the unperturbed magnon picture of the scattering begin to exhibit distortion (200 °C) — see figures 6, 8, 9, and 11 — is roughly the same (when expressed in the reduced temperature — \(T/T_0\)) as in Fe\(_3\)O\(_4\) [11] but seems rather independent of the q-value or effective energy of the magnon group. The effective exchange stiffness \(^{(4)}\) behaves roughly as the magnetization but certainly does not vanish in the critical point. This could be interpreted in favour of the concepts which extend the magnon or collective excitation picture to or even above the critical point [4], [7], [8]. However, it is better to say at present that the results for pyrrhotite reveal with certainty only the fact that in the investigated region of q-values the scattering does not lose its inelastic character even for temperatures close to the critical point.

It can be noted that the appearance of the observed inelastic scattering peaks is not in radical contradiction to the ones foreseen by the Van Hove treatment (formula (1)) based on the spin diffusion approximation and valid only in the limit of small q values. Recently Mori and Kawasaki [9] pointed out that the damping constant for longitudinal spin fluctuations can have a term (strongly q dependent) which does not vanish at \(T_0\).

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VI. Appendix. — One has to isolate the theoretical shape from the convolution of the ideal diffuse peak with the instrumental resolution function. The latter was taken in the two following forms:

$$T_{in}(x) = \begin{cases} 0 & \text{for } x > \Gamma_0/2 \\ -\frac{2B}{\Gamma_0} x + B & 0 < x < \Gamma_0/2 \\ +\frac{2B}{\Gamma_0} x + B & -\Gamma_0/2 < x < 0 \\ 0 & x < -\Gamma_0/2 \end{cases}$$  \hspace{1cm} \text{the triangle form}  \\
$$T_{in}(x) = B \exp \left\{ -\left(2x/\Gamma_0\right)^2 \right\} \text{the gaussian form (A1')}$$

\(^{(4)}\) Under the term " exchange stiffness " we understand the product \(J_{1/2}(S_8 - S_0)\), see [13].
where \( \alpha \) = angle between the axis of the collimator and direction of the neutron propagation,
\( B \) = constant of proportionality,
\( \Gamma_0 \) = total width of the resolution function,
\( \Gamma_0 = \frac{\Gamma_0}{2} \sqrt{\ln 2} \).

Because the array of counter with a wide detection angle in the vertical plane was used, it can be assumed that automatic integration of the intensity in this direction took place.

When the natural width of magnon lines is neglected, it was proved by means of numerical integration that the quasi \( \delta \)-shape (on the edges) angular distribution (see fig. A1-a) is transformed to a nearly rectangular one \( I_p(x) \) (this is valid for a not too high angular resolution) — see figure A1-b. If the width of the primary distribution \( I_p(x) \) is denoted by \( 2\alpha_0 = \Gamma_{\text{max}} \) and the height by \( A \), then the convolution of \( I_p(x) \) with \( T_{\text{in}}(x) \) (A1) for the case \( \alpha_0 > \frac{\Gamma_0}{2} \) gives the curve (A2) — see figure A1-c:

\[
I(\alpha) = \frac{A \cdot B}{2} \left( \frac{\Gamma_0}{2} - \left[ \alpha - \left( \frac{\alpha_0 + \Gamma_0}{2} \right) \right]^2 \right)
\]

for respectively
\[
\begin{align*}
\alpha &> \alpha_0 + \frac{\Gamma_0}{2} \\
\alpha_0 < \alpha < \alpha_0 + \frac{\Gamma_0}{2} \\
\alpha_0 + \frac{\Gamma_0}{2} < \alpha < \alpha_0 \\
0 < \alpha < \alpha_0 - \frac{\Gamma_0}{2}
\end{align*}
\]

It is easily seen that the widths \( \Gamma_{1/2c} \) at half of the peak height are equal \( 2\alpha_0 \) and that the tangent to the curve at this point cuts off on the abscissa axis the section \( \Gamma_s \) which differs from \( \Gamma_{1/2c} \) by
\[
\Delta \Gamma = \Gamma_s - \Gamma_{1/2c}
\]

Taking into account the natural width of magnon lines \( \gamma \), the resulting \( I_p(x) \) can be approximated by summing many rectangular distributions with heights changing as a certain probability function \( F(x) \). This means \( I_p(x) \) is given by (A4):

\[
I_p(x) = C \int_{-\infty}^{\infty} F(x) \, dx
\]

where \( C \) is a constant of proportionality. A Lorentz form (A6) of the function \( F(x) \), strictly valid for a linear dispersion law (A5), was assumed:

\[
\omega(q) = a + m \cdot q
\]

\[
F(x) = \frac{1}{\pi} \frac{1}{(x - \alpha_0)^2 + 1}^{-1}
\]

where
\[
\varepsilon = m \times k_c \gamma \quad k_c \text{ — see [15].}
\]

For the purpose of calculation the \( F(x) \) function was replaced by the triangular shape function — see figure A1-d — with total width \( 2\gamma \) equal 4.6\( k_c \).

Under the above-mentioned assumptions and condition \( \alpha_0 > \gamma \) the primary distribution \( I_p(x) \) has wings, being a quadratic function of the angle, and after convolution with (A1') the effective \( I(\alpha) \)
It can be shown that \( \Delta \Gamma \to \Gamma_0/2 \) for \( \lambda \to 0 \) and 
\[ \Delta \Gamma \to \frac{\Gamma_0}{2} \sqrt{\frac{\lambda}{\pi}} \text{ for } \lambda \to \infty. \]

So the dispersion law can be measured directly from (A8) and the magnon life time from (A10):

\[ \tau_{\text{mag}} \frac{df}{d\gamma} = 9.2\sqrt{\ln 2} \cdot \frac{1}{\lambda} f(m, k_e, \Gamma_0, \lambda). \]