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ESTUDO DA DIFUSÃO LOCALIZADA DO HIDROGÊNIO NO COMPOSTO $Ti_{0,8}Zr_{0,2}CrMnH_3$ POR MEIO DE ESPALHAMENTO QUASE ELÁSTICO DE NÊUTRONS LENTOS*

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RESUMO

A difusão localizada do hidrogênio no composto armazenador $Ti_{0,8}Zr_{0,2}CrMnH_3$ foi estudada por meio de espalhamento quase elástico de nêutrons lentos empregando o espectrômetro de filtro de berílio-tempo de vôo. Foi detectado um alargamento na linha quase elástica mais de uma ordem de grandeza superior ao encontrado no caso da difusão a longo alcance, numa situação experimental na qual o comprimento de correlação observado equivale à distância média de saltos na difusão do hidrogênio.

(*) Trabalho apresentado no "XI Encontro Nacional de Física da Matéria Condensada", realizado em Caxambú, MG, de 9 a 13 de maio de 1988.

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ABSTRACT

The localized diffusion of hydrogen in the storage compound $Ti_{0,8}Zr_{0,2}CrMnH_3$ was studied by quasielastic slow neutron scattering with the berilium-filter-time-of-flight spectrometer. A large quasielastic width was detected which is more than one order of magnitude larger than that observed for long range diffusion, in an experimental situation in which the observed correlation lenght was the same as the mean jump lenght for hydrogen diffusion.

(*) Paper present at the "11th Encontro Nacional de Física da Matéria Condensada", held in Caxambú, MG, May 9 - 13, 1988.

INTRODUCTION

The quasielastic neutron scattering technique (QNS) offers a possibility to study the diffusive motion of atoms on an atomic scale. A stricking feature of this technique that has no conterpart in other techniques is the possibility to observe both the long range diffusion and the details of locally elementary steps for diffusion(1).

In dealing with metal-hydrogen systems specially those with high hydrogen concentrations such as the materials developed for hydrogen storage pourposes(2), it was frequently observed that there are two time scales for diffusional motion of hydrogen, one for long range diffusion and another one, which is more than one order of magnitude smaller, for local diffusive steps(3-5).

These locally rapid hydrogen motions are not yet well understood(4) and are possible to be observed in a QNS experiment.

In this work we present a study of the hydrogen localized motions in the storage compound $Ti_{0,8}Zr_{0,2}CrMnH_3$ with QNS, utilizing a traditional berillium-filter-time-of-flight instrument.

In a QNS experiment, a monocromatic neutron beam impinges on the sample and an energy analysis of the scattered neutrons at a fixed scattering angle is performed. For metal-hydrogen systems, the scattering contribution from hydrogen is isolated, since the scattering cross section due to hydrogen is one order of magnitude higher than for other elements. The incoherent scattering cross section is given by(6):

$$\frac{d^2\sigma i}{d\Omega dE'} = N \frac{k'}{k} \frac{\sigma i}{4\pi} Si(\vec{Q},\omega) \qquad (1)$$

Where $\hbar\vec{Q} = \hbar(\vec{k} - k')$ is the momentun transfer on scattering while $\vec{k}$ and $\vec{k}'$ are the initial and final neutron wave vectors, respectivelly. $\hbar\omega = E - E'$ is the energy transfer on scattering. E and E' the initial and final neutron energies, respectivelly. Si is the incoherent scattering law and σi the incoherent microscopic scattering cross section for hydrogen.

The incoherent scattering law is related to a self correlation function $G_s(\vec{r},t)$ by a double Fourier transformation(6):

$$S_i(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \iint e^{i(\vec{Q}.\vec{r} - \omega t)} G_s(\vec{r},t)\, d\vec{r}\, dt \qquad (2)$$

In the classical jump diffusion model, originally proposed by Chudley and Elliott(7), it is assumed that the hydrogen performs a jump to a neighboring interstitial site after a mean time of stay on a site given by τ. The diffusion equation for such a model is described as(7):

$$\frac{\delta P(\vec{r})}{\delta t} = \frac{1}{n\tau} \sum_{\vec{\ell}} \left[P(\vec{r} + \vec{\ell}) - P(\vec{r}) \right] \qquad (3)$$

Where $P(\vec{r})d\vec{r}$ means the probability to find the hydrogen atom in the volume element $d\vec{r}$ pointed by the vector $\vec{r}$. n is the number of neighboring interstitial sites relative to one site and $\vec{\ell}$ are the vectors that define these neighboring sites.

The auto-correlation function $G_s(\vec{r},t)$ is obtained by solving equation 3 with the initial condition $G_s(\vec{r},o) = \delta(\vec{r})$. Performing also the transformation shown in equation 2, finaly one obtains the scattering law, given by:

$$S_i(\vec{Q},\omega) = \frac{1}{\pi\hbar} \frac{f(\vec{Q})}{|f(\vec{Q})|^2 + \omega^2} \qquad (4)$$

which is a lorentzian function centered at the energy transfer $\omega = o$, and a half width at half maximum $f(\vec{Q})$ given by:

$$f(\vec{Q}) = -\frac{1}{n\tau} \sum_{\vec{\ell}} \{e^{-i\vec{Q}.\vec{\ell}} - 1\} \qquad (5)$$

and frequently called the structure factor for diffusion. In the case of a isotropic distribution of a large number of sites, one has:

$$f(Q) = \frac{1}{\tau} \left(1 - \frac{\text{sen } Q\ell}{Q\ell}\right) \qquad (6)$$

which is also a good approximation when the experiment is performed in powder or policrystaline samples.

For small values of Q, we have:

$$\lim_{Q \to o} f(Q) = DQ^2 \tag{7}$$

Where $D = \ell^2/6\tau$ is the diffusion coefficient.

So, if one plots the width of the lorentzian scattering function against Q^2 for small values of Q, the slope of the strait line obtained gives directly the microscopic diffusion constant D, without any problems related with the surface cleanliness or grain boundaries, such as encountered in permeation methods. Furthermore, for larger values of Q, it is possible to determine the mean jump lenght ℓ in the diffusion process, a parameter that is impossible to extract by any other method. Even more details are possible to extract if one measure the lorentzian width in monocristals when a choice is made for a particular orientation of the scattering vector relative to the metal lattice.

In high hydrogen concentration materials, the hydrogen jumps are blocked due to the fact that most of the neighboring interstitial sites are already occupied by hydrogen atoms. After performing a jump, the interstitial atom has more chance to perform another jump back to the original position. Then, simultaneously with the relatively slow long range diffusional motion, the hydrogen atom may perform various rapid localized jumps between two neighboring interstitial sites. It is expected that the mean time of stay for this motion τ_R, will resemble that of a diffusional motion in dilute case, and so, $\tau_R<\tau$.

We made a simple ansatz to take into account this type of motion.

It was assumed that the corresponding self correlation function is given by:

$$G_s^R(\vec{r},t) = \frac{1 + e^{-t/\tau_R}}{2}\,\delta(\vec{r}) + \frac{1 - e^{-t/\tau_R}}{2}\,\delta(\vec{r}-\vec{a}) \tag{8}$$

Where $\vec{a}$ represents a vector pointing to one neighbor position relative to $\vec{r} = o$. So, for $t = o$, the particle is at the origin $\vec{r} = o$. The probability to find the particle here decreases with time at the same rate that the probability to find it at a position $\vec{r} = \vec{a}$ increases with time. For $t \to oo$ the probability to find a particle is the same for both positions $\vec{r} = o$ and $\vec{r} = a$.

Assuming furthermore that the distribution of vectors $\vec{a}$ is isotropic and making the transformation given by equation (2), one gets:

$$S_i^R(Q,\omega) = \frac{1}{2\pi\hbar}\,\frac{1/\tau_R}{(1/\tau_R)^2 + \omega^2}\,\frac{1 - \text{sen } Qa}{Qa} + \frac{1}{2\hbar}\,\delta(\omega)\,\frac{1 + \text{sen } Qa}{Qa} \qquad (9)$$

It is readilly seen that the scattering law has in this case two lorentzian components: one with a fixed and large width $1/\tau_R$ and another one without inelastic scattering, given by $\delta(\omega)$. The intensity of the former component increases with Q whereas the intensity of the other decreases with Q by the same amount. Note that in this case it is the intensity that varies with Q, in contrast to the situation given by equation (4) where it is the width that varies with Q. This is the way by which the rapid localized motion can be completely caracterized and isolated from the long range diffusional motion.

In going further, we must take into account the both type of diffusional motion, i.e., the localized and long range diffusion and also the vibrational motions. The result of this step is that the resulting scattering law is the convolution of equation (9) with equation (4), so that we have already two components: one given by equation (4) instead of $\delta(\omega)$ and another one given by a lorentzian function the width of which is a sum $f(\vec{Q}) + 1/\tau_R$, and can be approximated by $1/\tau_R$. Convolution with the vibrational scattering law introduces a Debye-Waller intensity factor governing both the components(6), giving the final result:

$$S_i(Q,\omega) = \frac{e^{-2W(Q)}}{2\pi\hbar}\left[1 + \frac{\text{sen } Qa}{Qa}\right]\frac{f(\vec{Q})}{|f(\vec{Q})|^2 + \omega^2} +$$

$$+ \frac{1/\tau_R}{(1/\tau_R)^2 + \omega^2}\left[\frac{1 - \text{sen } Qa}{Qa}\right] \qquad (10)$$

EXPERIMENTAL DETAILS AND RESULTS

The $Ti_{0,8}Zr_{0,2}CrMnH_3$ intermetallic compound was produced by Gesellschaft fur Electrometallurgie, Nurnberg, west Germany, and the method of preparation is described elsewere(8). Hydrogenation was parformed in our laboratory by a direct reaction of the metallic alloy with hydrogen gas (99.99% purity), utilizing a specially developed stainless-steel reactor. Three cycles of charging-discharging were sufficient to give a uniform hydride sample, which was then sealed with a thin oxide layer by a slow reaction with oxigen at 77K(8). The amount of absorbed hydrogen was determined by a controlled extraction of hydrogen at 870K in a fraction of previously prepared sample. An X-ray diffraction pattern was obtained in order to confirm the existence of only one hydride phase. No unreacted material was detected(9).

The powder sample was introduced in an aluminium container with dimensions 9.5 X 4.5 X 0,025 cm^3 and with 0,1 cm wall tickness. The sample transmission was 85% for 4.8 Å neutrons.

The neutron spectrometer utilized in this work is a traditional Be--filter-time-of-flight spectrometer instaled in a beam port of a material testing swimming-pool reactor at IPEN-SP(10). The incident neutron spectrum is centered at 3.5 meV and is 2 meV wide (FWHM). The overall resolution for 5.12 meV neutrons (Be cut-off) is 150 μeV(FWHM).

Several spectra were recorded with the sample in the temperature range of 299 K to 398 K and scattering angle in the range of 25 to 90 degrees.

Figure 1 shows a tipical raw spectrum obtained. It consists mainly of three distributions of scattered neutrons. The first one is centered around channel number 40 representing neutrons that exchanged about 100 meV of energy and are due to localized hydrogen vibrations, and was analysed elsewere(11). The second distribution, around channel number 100, represent the band modes of the metallic lattice, with which the Debye temperature of the $Ti_{0,8}Zr_{0,2}CrMnH_3$ compound, was obtained, giving $\Theta_D = 311 \pm 10$ K(9). The other distribution around channel 200 is due to the quasielastic scattering of neutrons and is effectivelly the subject of this work.

Several corrections were made to the raw data prior to the analysis of the width introduced by quasielastic neutron scattering on hydrogen. Firstly the contribution from scattering on the metallic part of the sample and on the aluminium container was subtracted. Also the background conting was subtracted(9). Afterwards the spectra were corrected for chopper transmission(10), detector efficiency and absorption/ /scattering by air.

A method was spetially developped for the analysis of the quasielastic width, which consis: of the folowing steps:

1) A spectrum of the incident beam was obtained with the time-of-flight spectrometer positioned at 0 degrees.

2) The incident beam spectrum was numerically convoluted with a gaussian function. The width of the gaussian function was adjusted such that the resulting convoluted spectrum had the better fit to a spectrum obtained with a vanadium sample at a temperature of 299 K and 45 ° degrees scattering angle. So, a very precise spectrum that represents the purely elastic scattering was obtained. The observed width in this spectrum, measured by the slope of the bragg cut-off due to berilium, represents the resolution of the time-of-flight spectrometer which is 150 μeV(FWHM)(12).

3) The spectrum obtained in step 2 was numerically convoluted with a function that is a lorentzian in an energy scale. Several spectra were calculated in this way the widths of which were in the range from 1 μeV to 50 μeV. A specially designed computer code was necessary to perform the numerical convolutions(9). These spectra were then fitted to the experimental data, one by one, taking as a adjustable parameter, only the intensity of the spectra. Only 30 channels around the Bragg cut-off were considered. The width of the quasielastic line was determined by the choice of the spectrum which resulted in the best fit to the experimental data. It was impossible to adjust two components to any experimental spectrum due to the relatively wide distribution of incident neutrons.

Figures 2 and 3 show the results of the quasielastic scattering from hydrogen in $Ti_{0,8}Zr_{0,2}CrMnH_3$. The full curves in these figures are the result of the fitting procedure outlined above. Only the spectrum obtained at a temperature of 398 K and scattering angle 86 ° (figure 3) has a quasielastic width of 15 ± 6 μeV whereas the spectra for temperature of 299 K (figure 2), and all the others spectra, no present any observable width within our experimental errors. It is possible to observe the presence of the quasielastic widening in figure 3: the rise of the Bragg cut-off in this case is less steep than that of figure 2. Also the effect of the Pb cut- above the Be cut-off, is less pronounced in figure 3 than in figure 2.

DISCUSSION

In the present work it was not possible to isolate the quasielastic line due only to the rapid localized motions of hydrogen $Ti_{0,8}Zr_{0,2}CrMnH_3$. The caracterization of these motions needs a separation of the quasielastic line into two components, as predicted by equation (10). Nevertheless, it was possible to detect the presence of the rapid localized motions by the observation of an effective quasielastic width that is more than one order of magnitude larger than that observed for a long range diffusional motion which is nearly 0,5 $\mu eV^{(8)}$. This means that the mean time of stay for long range diffusion at 398 K is $\tau_0 \sim 3 \times 10^{-10}$ s whereas the mean time of staly for local diffusion, at the same temperature, is $\tau_R \sim 10^{-11}$ s.

Furthermore, this large width was observed for a scattering vector $Q = 2.1$ Å^{-1} which gives a correlation lenght $< r > = 3$ Å that is nearly the same as the mean jump lenght for hydrogen diffusion in the compound $Ti_{0,8}Zr_{0,2}CrMnH_3$ ($\ell = 2,8 \div 4$ Å)$^{(8)}$. This means that for Q values larger than 2.1 Å^{-1}, only a fraction of a diffusion lenght is experimentaly observed, giving a quasielastic width that depends strongly on the local jump frequency.

For a complete analysis of this motion, an experiment with more resolution in energy is needed. This may be accomplished simply by using a narrower incident line than that used in this work. This problem is of interest since it is expected that by this way it is possible to estimate the activation energy for diffusion by observation of the localized motions istead of the long range diffusion which needs an experiment with very high resolution, difficult to obtain with medium flux reactors.

CONCLUSION

In spite of the fact that it was not possible to isolate the com ponent of the quasielastic line due to local hydrogen diffusion on $Ti_{0,8}Zr_{0,2}CrMnH_3$, we were able to detect the existence of these local motions.

The main problem in this experiment is the relatively large distribution of incident neutrons, and it seems that another experiment with a narrower distribution will make possible a full caracterization of the rapid localized motions of hydrogen in this or another compound. Furthermore we believe that, by studying these motions it is possible to obtain the three important parameters which are often determined through the analysis of the long range diffusion: the mean jump lenght, the mean time of stay and the activation energy for diffusion.

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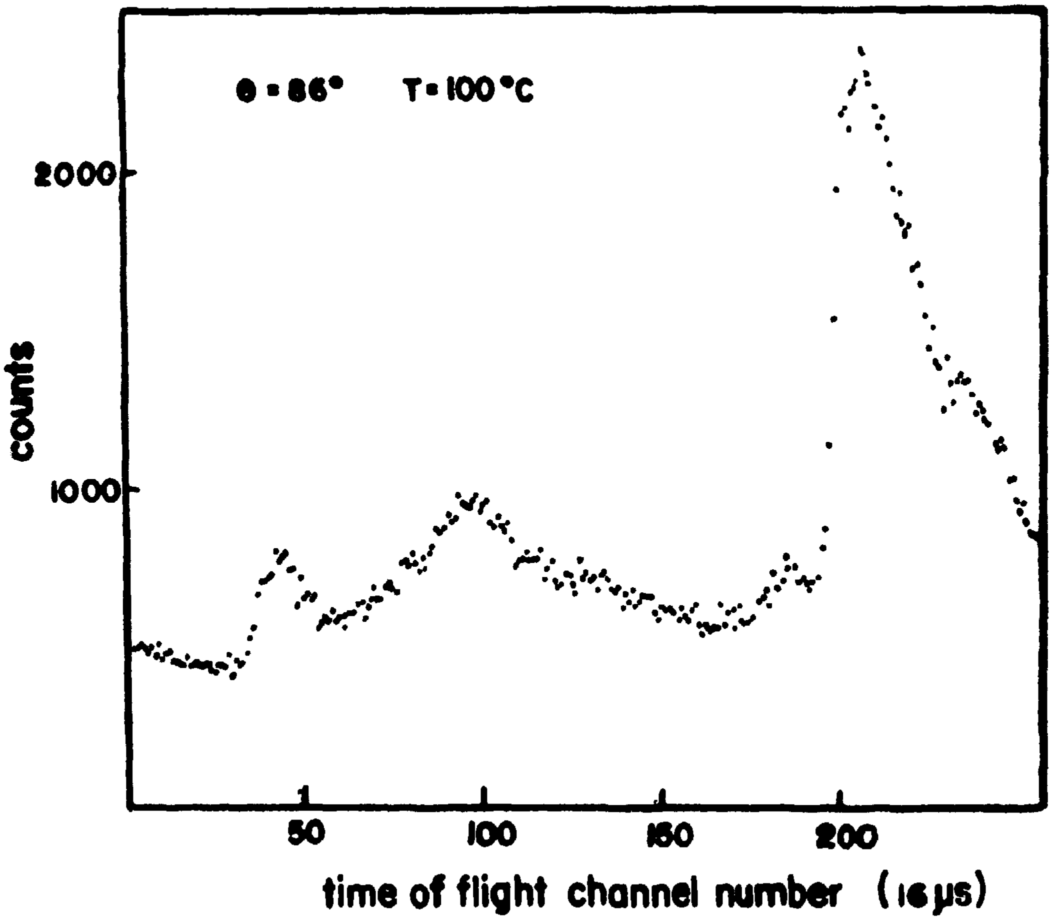

Figure 1:

Time of flight distribution of neutrons scattered on $Ti_{0,8}Zr_{0,2}CrMnH_3$ at 86 degrees scattering angle and 373 K sample temperature. Flight path = 3.15 m. Time per channel = 16 μs.

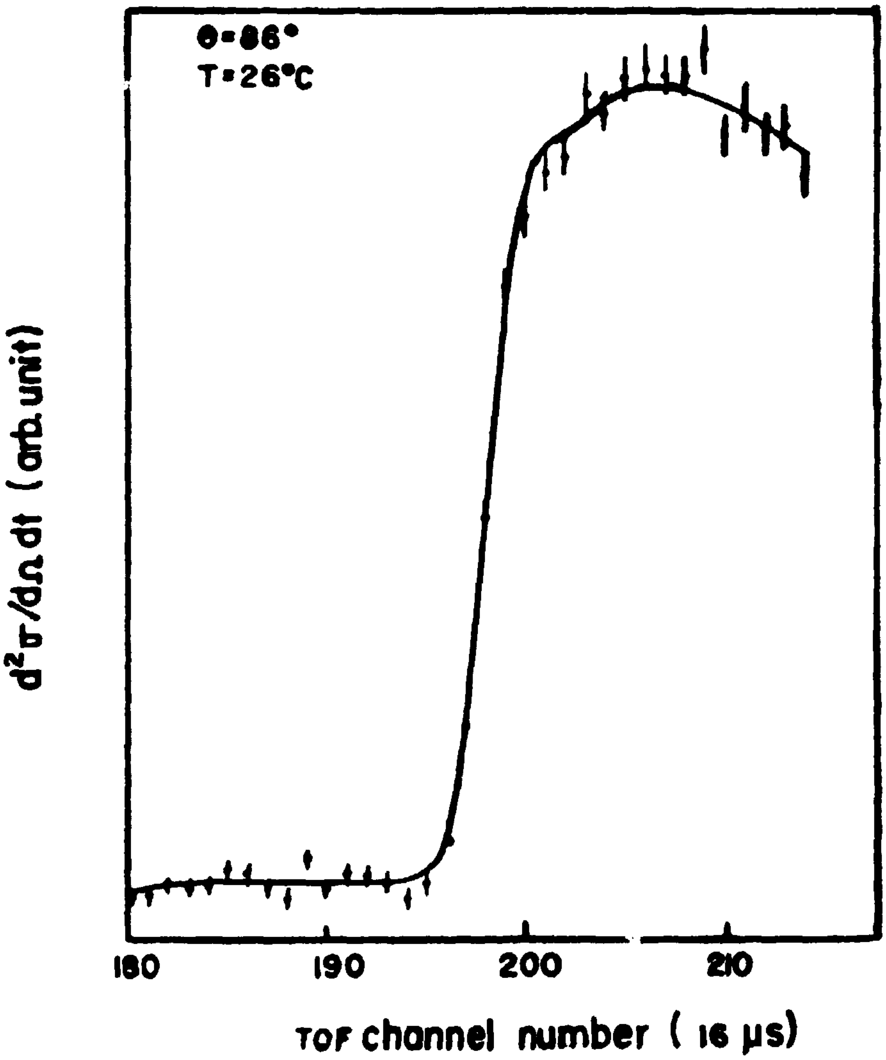

Figure 2:

Time of flight distribution of neutrons scattered quasielasticaly on $Ti_{0,8}Zr_{0,2}CrMnH_3$ at 86 degrees scattering angle and 299 K sample temperature. Full curve = result of a fit of the elastic line to data points (no broadening).

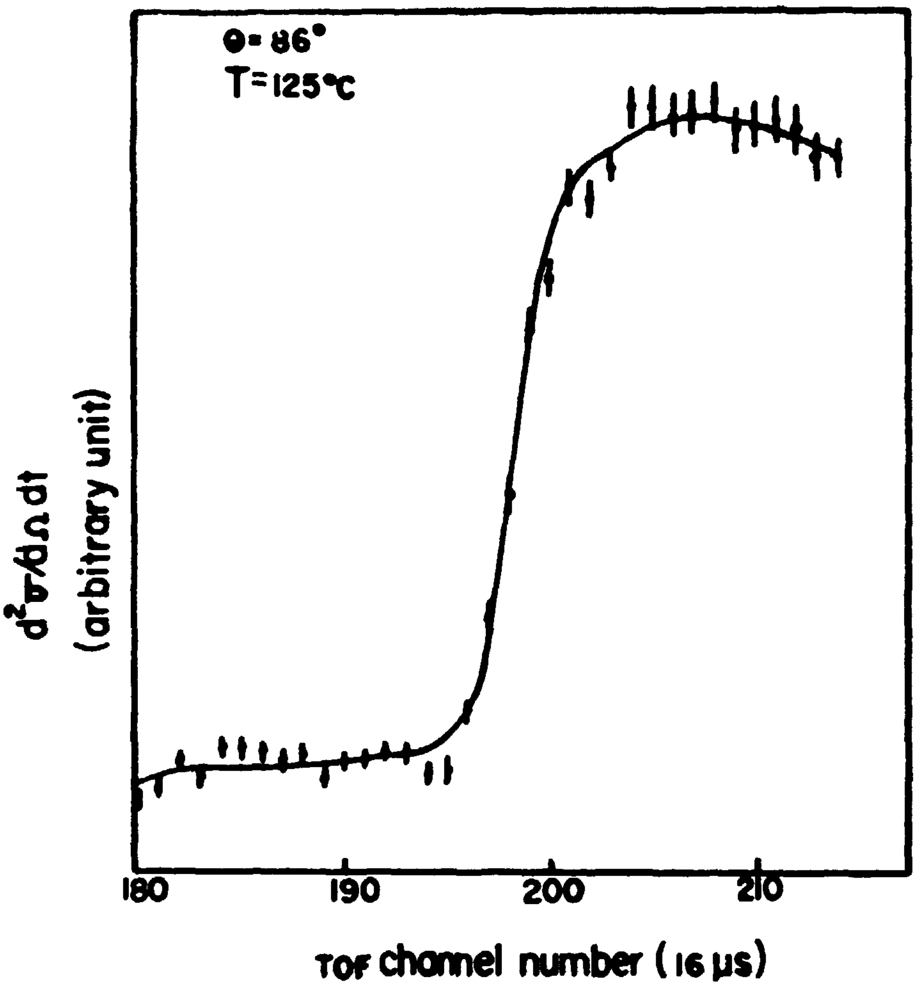

Figure 3:

Time of flight distribution of neutrons scattered quasielasticaly on $Ti_{0,8}Zr_{0,2}CrMnH_3$ at 86 degrees scattering angle and 398 K sample temperature. Full curve = result of a fit of the elastic line convoluted with a 15 μeV half width half maximum lorentzian curve.