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Magnetic diffuse and small-angle scattering

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Magnetic neutron scattering is one of the most valuable tools in exploring magnetism. For disordered magnetic systems, in addition to Bragg scattering, diffuse and small-angle scattering give information. Experimental techniques of the two last mentioned methods are described. They succeeded in a microscopic explanation of magnetic alloys with paramagnetic, spin-glass, ferromagnetic and antiferromagnetic character. Typical examples will be discussed in detail. Non-frozen local magnetic moments show quasi-elastic scattering, the half-width of which is a characteristic for the relaxation processes. By diffuse inelastic neutron scattering the temperature dependence and concentration dependence of such relaxation processes have been studied for classical paramagnetic, Kondo- and intermediate-valence systems. An additional impact to the field is to be expected from new developments of polarization analysis techniques.

1. Introduction

The number of scattering studies of disordered structures has rapidly increased within the last decade for two reasons: (i) the improvement of experimental techniques, especially at high flux reactors, now allows detection of weak scattering intensities; and (ii) solid state physicists have become more interested in disordered structures. With neutron small-angle and diffuse scattering, information on spatial correlations both on a long-range and a local atomic scale is obtained. This holds for both nuclear and magnetic thermal neutron scattering. Though this lecture deals only with magnetic small-angle and diffuse scattering, the subject is too broad to be discussed in detail. Therefore emphasis will be given to the underlying general aspects, followed by four short specific sections. I have recently reviewed the subject (Schmatz 1978). Only some very recent developments will be referred to here in addition.

2. General aspects

In magnetic neutron scattering, the relevant interaction operator is $\boldsymbol{\mu}_n \cdot \boldsymbol{B}$, where $\boldsymbol{\mu}_n$ is the neutron magnetic moment – a product of the absolute value of $\boldsymbol{\mu}_n$ and the Pauli spin matrices – and $\boldsymbol{B}$ the operator of magnetic induction of the scattering system. The scattering formalism shows that in a scattering experiment the Fourier transform of the space- and time-correlation of the local magnetic moments is measured as a function of the momentum transfer $\hbar Q$ and the energy transfer $\hbar\omega$ to the scattering system. The scattering is, however, also a function of the initial neutron spin polarization $\boldsymbol{p}_0$ via $\boldsymbol{\mu}_n \boldsymbol{B}$. For instance, with $\boldsymbol{p}_0 = \boldsymbol{0}$ no interference terms between nuclear and magnetic scattering appear in the scattering intensity, whereas the intensity can be altered considerably by varying $\boldsymbol{p}_0 \neq \boldsymbol{0}$ both in direction and absolute magnitude. Even more information can be obtained in magnetic neutron scattering if in addition to the scattering intensity the polarization $\boldsymbol{p}_1$ of the scattered beam as a function of

$\boldsymbol{Q}$, ω and $\boldsymbol{p}_0$ is determined. But, with a few exceptions, this additional source of information is very little explored today even where it would be essential for the problem under investigation. To get $\boldsymbol{p}_1$ requires considerable effort and it is a real challenge to develop more suitable techniques for the polarization analysis of scattered neutron beams. Possibly the mass production of supermirrors is an essential basis for new devices.

Another general aspect to be considered within our topic is the limit of scattering theory in first Born approximation. This approximation requires that an inhomogeneity will attenuate the traversing beam only by a fraction much smaller than unity. This holds if the total scattering cross section σ_{tot} is much smaller than the geometrical cross section σ_{geom}. Now (assuming a spherical inhomogeneity), it can easily be shown that σ_{tot} increases with the fourth power of the diameter D of the inhomogeneity whereas the geometrical cross section is proportional to D^2. This means for large inhomogeneities ($\sigma_{\text{tot}} > \sigma_{\text{geom}}$), a much more complicated scattering theory is necessary. Only for very large scattering objects does one return to a simple theory (geometrical optics) again.

For the discussion of the various possibilities of scattering experiments on disordered structures, a subdivision of reciprocal space ($\boldsymbol{Q}$-space) is reasonable. At first, we have to consider the immediate neighbourhood of $\boldsymbol{Q} = \boldsymbol{0}$ and $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$, where $\boldsymbol{\tau}_{hkl}$ is the reciprocal lattice vector for the reflecting plane hkl. Within a radius of 10^{-4} Å^{-1}† around these points large inhomogeneities as grain boundaries, magnetic domain walls and surface inhomogeneities may give scattering intensity in this region, which can be accompanied also by neutron depolarization. The scattering effects are rather strong and thus for $\boldsymbol{Q} = \boldsymbol{0}$ scattering multiple scattering may occur, which may extend the scattering effects of such large inhomogeneities up to effective scattering vectors of $Q = 10^{-2}$ Å^{-1} in extreme cases. We name this region of variable extension the 'nearby $\boldsymbol{Q} = \boldsymbol{0}$' region. Small-angle neutron scattering (s.a.n.s.) in its original sense was meant as scattering performed under small scattering angles. We define s.a.n.s. in this context as scattering that can be interpreted in first Born approximation for Q values between 10^{-4} Å^{-1} and 0.3 Å^{-1}. The lower limit is somewhat arbitrarily determined by the best resolution obtainable today. The upper limit is reasonable because for much larger Q values the local atomic arrangements has to be considered in calculating scattering cross sections, whereas in s.a.n.s. theory one prefers to define a density of scattering lengths as an average value for some hundreds of atoms. The nearby $Q = 0$ region as defined above and the s.a.n.s region may overlap, but this makes sense because they are defined for quite different scattering phenomena. The total $\boldsymbol{Q}$ region except the nearby $\boldsymbol{Q} = \boldsymbol{0}$ (and the nearby $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$) region can be regarded as the region of diffuse neutron scattering (d.n.s.). However, having in mind that diffuse scattering, as originated by more or less randomly distributed local atomic fluctuations, is normally very weak, one knows from experimental experience that this region can hardly be explored very near to $\boldsymbol{Q} = \boldsymbol{0}$ or $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$. First, the low intensities require mostly large resolution elements in $\boldsymbol{Q}$-space ($\Delta \boldsymbol{Q} \approx 0.1$ Å^{-1}) and in the experiment it is absolutely necessary not to include $\boldsymbol{Q} = \boldsymbol{0}$ or $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$ even with the slightest tail of the resolution distribution around the average $\boldsymbol{Q}$ value. Secondly, near $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$, the reciprocal lattice point may be extended considerably by azimuthal mosaic spread. And finally, near $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$, low frequency phonons may be emitted or absorbed by the incident neutrons with a rather high scattering cross section, which gives a considerable background intensity. Thus diffuse scattering

† 1 Å = 10^{-10} m = 10^{-1} nm.

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is normally performed at least at a distance of 0.1 $Å^{-1}$ from $\boldsymbol{Q} = \boldsymbol{0}$ or $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl}$. There are, however, special cases in which it is worthwhile to go very near to the reciprocal lattice points; for instance in studies of critical scattering or if long range lattice distortions are of interest.

The last general aspect to be discussed is the separation of elastic and inelastic scattering. S.a.n.s. and d.n.s. are often performed without any energy analysis of the scattered beam. The 'Q-dependent' scattering pattern is obtained as a 'snapshot' with an aperture opening time of $\hbar/E_0$, where E_0 is the energy of the incident neutron beam. The $|Q| - \omega$ relation for a fixed scattering θ, however, makes it quite uncertain for what average Q value the snapshot has been taken for a given scattering angle. We have to be sure that the scattering is preferentially concentrated around $\omega = 0$ in an interval $\Delta\omega$ much smaller than $E_0/\hbar$. Then Q is, to good approximation, $4\pi\lambda^{-1} \sin\theta$, where λ is the neutron wavelength. Otherwise we have to perform an energy analysis of the scattered beam. In nuclear scattering, the condition above is normally fulfilled rather well for the 'elastic' scattering of disordered structures. (Only in a few cases, e.g. for hydrogen diffusion in metals, does one have to be careful.) Magnetic moments, however, have often short relaxation times for spin diffusion and there are really extreme cases, as we shall see in §6.

3. Zero beam experiments

One of the simplest neutron scattering experiments is given by the transmission of a well collimated beam through a demagnetized slab of magnetically soft iron containing many magnetic domains along the neutron path. The beam is broadened by multiple refraction and this broadening can easily be measured with a detector at a sufficient distance. With slit geometry, even in low flux reactors the intensity for such an experiment is high enough. The most intensive study of a zero beam case has been performed within the last few years by Schärpf (1977). Neutrons enter ferromagnetic nickel with a well defined magnetic domain structure. The solution of the Schrödinger equation in the domain wall is based on four fundamental solutions, which in the general case are linearly combined with four times two coefficients (phases and amplitudes) to make the final neutron wave according to the boundary conditions. The results, e.g. the transmission coefficient, depend sensitively on the Bloch wall parameters. A small-angle scattering apparatus with very high resolution (2″), consisting of two parallel silicon monochromators with the sample between, was used to measure the separation of transmitted and deflected beam. The deflexion angle α (figure 1*a*) decreases with the tilt angle θ (figure 1*b*). The qualitative explanation is straightforward: the neutron path in the Bloch wall (thickness 200 Å) decreases with increasing θ.

Depolarization of the zero beam has been used to study characteristic parameters of domain walls and also for the analysis of inhomogeneous magnetization distribution in type II superconductors with pinning forces. The depolarization direction can be reversed rather rapidly with spin flippers. In two recent experiments, transient phenomena in zero beam neutron depolarization have been studied by this promising technique. Rekveldt & van Schaik (1979) observed single domain-walls on motion in a FeSi (3.5% by mass) picture frame crystal. Badurek *et al.* (1979) also applied this technique for the observation of magnetic after-effects, e.g. in the superparamagnetic alloy Cu–1% Co.

4. Neutron small-angle scattering

A consequent design with regard to luminosity and resolution considerations has led (1968–69) to the construction of the D 11 s.a.n.s. apparatus at the Institut Laue–Langevin (I.L.L.), which still can be regarded as the most powerful instrument of this type in the world. The incident neutron wavelength can be varied between 5 and 20 Å with a wavelength resolution, $\Delta\lambda/\lambda$, of either 10 or 30 %. The collimator entrance aperture and multi-detector can be a maximum distance of 40 m from the sample. For studies with lower resolution they are moved symmetrically towards the sample to a minimum distance of 1 m. Thus the accessible Q range is roughly

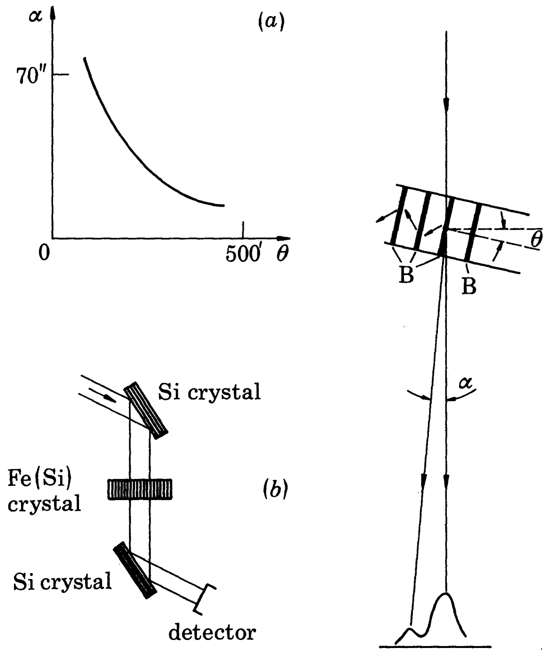

Figure 1. (*a*) Decrease of deflexion angle, α, with tilt angle, θ. (*b*) Illustration for α and θ; B are 90° Bloch walls (Schärpf 1977).

between 2×10^{-4} Å^{-1} and 0.3 Å^{-1}. The two-dimensional quadratic multi-detector with about 64×64 elements of size 1 cm^2 allows the simultaneous registration of the scattering for about 4000 Q values, which is of special value for anisotropic scattering patterns. The sensitivity may be characterized by the following statement: at D 11 a volume fraction of 10^{-4} of magnetic precipitates with a size of 300 Å is easily detectable in a sample of 1 cm^3. Additional counters (D 11B) in a circle around a special sample position can be used to get the diffuse scattering simultaneously. The D 11 instrument was shared between solid state physics, material scientists, chemists and biologists and thus a heavy overload resulted. Part of the burden at the I.L.L. has been taken over by a second instrument (D 17), constructed along the same principal lines but with slight modifications. There are similar or simpler instruments also at many other places (especially in west Europe), which together with D 11 and D 17 offer good possibilities in s.a.n.s. for the scientific community.

For magnetic scattering work it would be desirable to have polarized neutron beams or even the possibility of polarization analysis at the s.a.n.s. instruments. The former addition may be realized by a proper supermirror set-up. To get the addition of polarization analysis is certainly a more serious problem, if one would like to keep the multi-detector. A possible solution would be a nuclear polarization filter just behind the sample, if the filter could be produced in such a quality that no beam broadening or small-angle scattering arises from it. For more details on s.a.n.s. techniques the reader is referred to the recent review article by Schelten & Hendricks (1978).

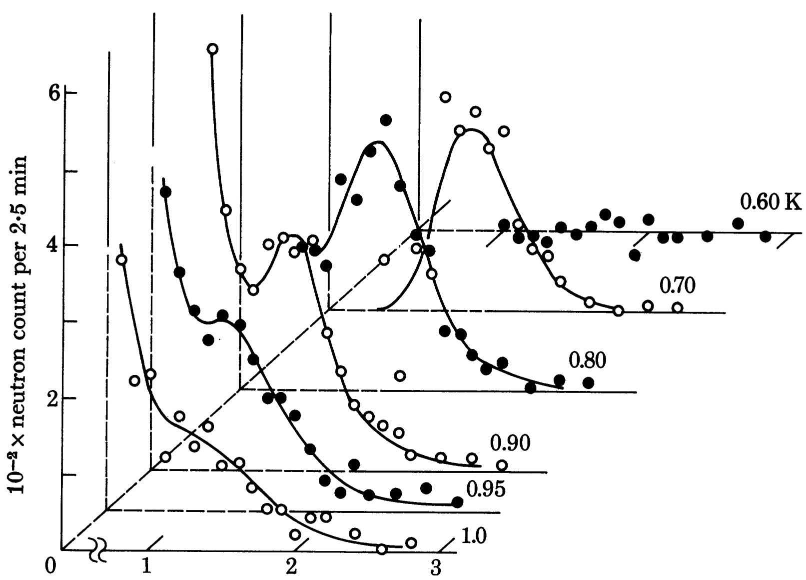

FIGURE 2. S.a.n.s. intensities of $ErRh_4B_4$ in the superconducting and low-temperature normal state (0.6 K) as a function of scattering angle 2θ and temperature (Moncton *et al.* 1979). The peak, corresponding to about 100 Å inhomogenity wavelength, is probably due to a helical magnetic structure.

A large variety of long-range magnetic fluctuations have been studied by neutron small-angle scattering: flux line lattices in type II superconducters, critical fluctuations in ferromagnets, superparamagnetic precipitates, precipitates in hard magnetic materials, dislocation strain induced fluctuations in cold-worked Ni and Fe near magnetic saturation, and magnetic fluctuations in the FeNi Invar alloy both as a function of concentration and temperature. Among the most recent studies the successful search for magnetic fluctuations in superconductors in the superconducting state should be mentioned especially (figure 2) (Moncton *et al.* 1979; Lynn & Glinka 1979).

5. MAGNETIC DIFFUSE SCATTERING

A typical magnetic scattering cross section for a binary alloy of about 1:1 ratio for the magnetic to non-magnetic component is 0.1–0.2 b/sr per atom†. This is well above the scattering cross section for coherent one-phonon scattering. Thus many studies for highly concentrated systems can be performed at normal two-axis diffractometer, and, if desirable, on triple-axis spectrometers and/or time-of-flight spectrometers. An essential drawback, however, is the unavoidable background due to nuclear incoherent elastic and nuclear elastic

† 1 barn (b) = 10^{-28} m².

disorder scattering. Depending on the system, there are favourable and extremely unfavourable systems. Also, in polarized beam experiments the nuclear scattering background reduces the statistical accuracy, and polarization analysis with a triple-axis spectrometer is at the very intensity limits. Nevertheless with 'normal' scattering techniques a considerable amount of work has been performed, especially by the Oak Ridge group.

What are the possible improvements? Diffuse scattering varies slowly with Q. This allows the use of large solid angles for the detector, multi-counter banks or multi-detectors can be installed, or the energy and angular resolution of the incident beam can be relaxed. Further, having a multi-detector reduction of inelastic background can in many cases be achieved by a low resolution time-of-flight technique. For instance, MAGS I at the FR2 in Karlsruhe is an instrument operating in this way. It is also no major problem to have an incident polarized beam in such an instrument. However, the only low-resolution spectrometer for diffuse scattering of thermal neutrons with polarization analysis is Longpol at Lucas Heights, at which iron transmission filters are used to guarantee large solid angles.

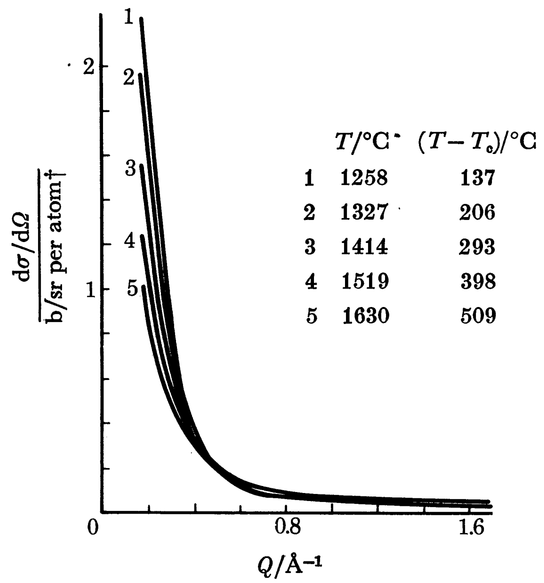

FIGURE 3. Diffuse scattering from magnetic clusters in cobalt below and above the melting temperature, T_m = 1493 °C (Rainer-Harbach 1979). † 1 barn (b) = 10^{-28} m^2.

An essential step towards higher intensity was achieved by the use of long-wavelength neutrons. Though the investigable Q-space is restricted for many magnetic systems, sufficient information can be obtained. The Harwell-glopper with a Be-filtered beam, a low resolution chopper and a detector bank was extremely successful in providing magnetic form factors for dilute alloys with a ferromagnetic matrix. The D 7 spectrometer at the cold source of the H.F.R. in Grenoble is at present the instrument with highest sensitivity for diffuse magnetic scattering. It can be operated either with an unpolarized or with a polarized incident neutron beam, and has been used in both modes of operation successfully for many problems of magnetic disorder. A further development would be the addition of polarization analysis. A supermirror system for such an addition is under consideration now. As long as diffuse scattering studies can be performed with neutron wavelengths not shorter than 4 Å, instruments at cold sources are superior to those at thermal beams. To obtain optimum conditions for $\lambda > 4$ Å should be the major task in near future. Nevertheless, considered within a long-term policy, the situation also has to be improved for thermal neutrons; for polycrystalline materials and amorphous substances this is absolutely necessary.

Among the many investigations in diffuse magnetic scattering the most spectacular result, to my mind, was the analysis of the giant moment induced by iron in palladium. Also a very remarkable result was the series of measurements to determine the magnetic form of dilute substitutional atoms in ferromagnetic matrices also performed mainly by the Harwell group. Concentrated alloys have been studied to see whether the magnetic form factor remains even on dilution with non-magnetic atoms. An extreme case where this fails is given for NiCu alloys. By comparison of the nuclear with the magnetic disorder scattering cross section, a magnetic disturbance for the nearest neighbours of Cu (at 10 % Cu) and magnetic disturbances up to fourth nearest neighbour shells for high Cu concentrations (40 %) could be deduced. Nowadays, magnetic short-range order of spin-glass systems and systems at the ferromagnetic side of the percolation limit are of high interest. Another remarkable result obtained recently was the successful search for small magnetic clusters in molten Fe and Co (figure 3). By careful experiments with $\lambda = 0.7$ Å neutrons and proper corrections for spin dynamics for the magnetic clusters in Co 100 K above the melting temperature, a correlation length of $\zeta = 2.8$ Å was obtained, a value in good agreement with that expected by extrapolation from critical scattering (Rainer-Harbach 1979).

6. Inelastic magnetic diffuse scattering

It has been well known for many years that well above the Néel or Curie temperature, well localized moments have a time-dependent correlation function, $\langle \boldsymbol{m}_i(0)\, \boldsymbol{m}_i(t)\rangle \approx \exp(-t/\tau)$. Thus at high Q values we have quasielastic magnetic scattering described by a frequency spectrum proportional to $\omega_m/(\omega^2+\omega_m^2)$, where $\omega_m = 1/\tau$. For small Q values, the neutron samples a larger region in real space and if there are many magnetic atoms within this region an excess magnetic moment diffuses more slowly out of this region than from a single site. ω_m becomes smaller; actually it becomes proportional to Q^2.

Recently the interest for spin diffusion has arisen again with all the studies of dilute magnetic moments in metals. For well behaved magnetic moments like Mn in Cu at high temperatures, or Fe in Au above the spin glass freezing temperature and also for many dilute 4f magnetic moments in metallic 4f compounds, $\boldsymbol{Q}$-independent values of ω_m have been measured that are proportional to the temperature, the typical so-called Korringa behaviour. Depending on the coupling, $\hbar\omega_m(T)$ ranges between a small percentage and an appreciable amount of $k_B T$. For 3d magnetic impurities in non-magnetic metals like Cu and Au at very dilute concentrations, Kondo condensation may happen (e.g. Fe in Cu). Then $\hbar\omega_m$ tends to become constant with $T \rightarrow 0$, thus crossing the $k_B T$ line in an $\hbar\omega_m$–$k_B T$ diagram (figure 4*a*). The scattering cross section given above has to be multiplied by the detailed balance factor $\hbar\omega/(1-\exp(-\hbar\omega/k_B T))$ whereby with the proper normalization factor the energy-integrated scattering cross section remains approximately constant. At $k_B T < \hbar\omega_m$ this results in a diffuse magnetic scattering cross section, which is off-centred from $\omega = 0$ (figure 4*b*)! For a Kondo system, which requires very low concentrations, this behaviour is on the limits of observability. Nevertheless Loewenhaupt got some reasonable results with 480 Fe/10^6 in Cu! Much easier is the situation for intermediate valence systems, which show similar cross-over behaviour because the atomic concentration is here about 10–25 %, and cross-over points occur at temperatures between 30 K ($Ce_2Cu_2Si_2$) and 300 K ($CeSn_3$) as far as investigations have been performed (Loewenhaupt & Holland-Moritz 1979). Such 'quasi-elastic' excitations seem also to exist for spin glasses below the freezing temperature, as observed recently for $Cu_{0.95}Mn_{0.05}$ with $\hbar\omega_m = 2.5$ meV, $k_B T = 4$ meV and $k_B T_f = 3$ meV (Scheuer *et al.* 1979). In interpreting the frequency spectrum with a single Lorentzian, caution seems to be necessary because of the restricted ω range normally applied. A recent experiment of Mezei & Murani (1979) with the neutron spin echo method demonstrated this clearly. With this technique, the time-dependent magnetic moment correlation function has been directly measured over a time scale of four orders of magnitude and it was evident that the data could not be interpreted by a single relaxation rate.

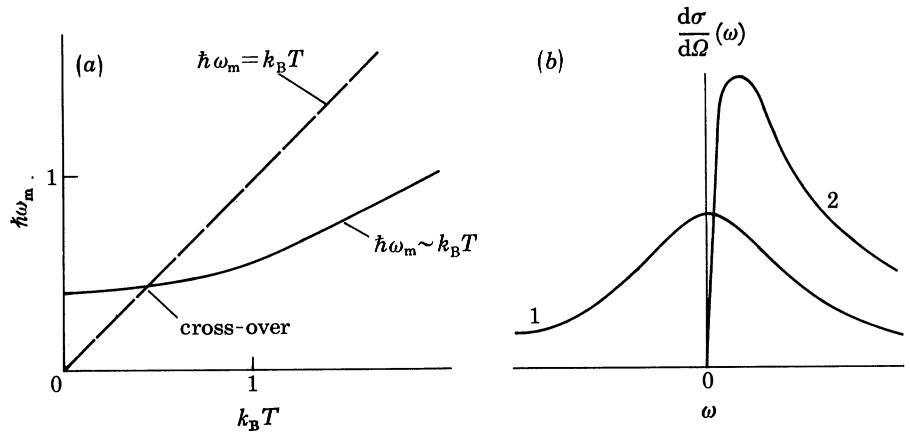

FIGURE 4. Schematic illustration for condensation of quasielastic scattering into an excitation-like, 'quasielastic' scattering for cross-over systems: (*a*) ω_m as a function of T; (*b*) frequency dependence of the scattering cross section for $\hbar\omega_m \ll k_B T$ (curve 1) and for $T = 0$ (curve 2).

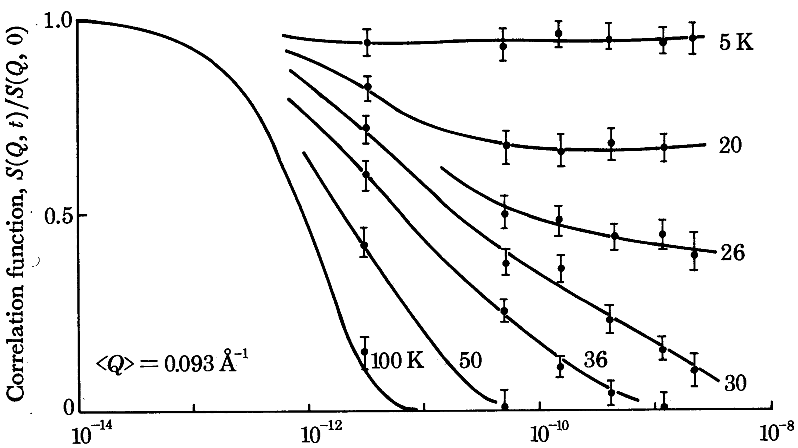

FIGURE 5. Time-dependent spin correlation functions of a Cu–5 at. % Mn spin glass as a function of temperature. Solid line, exponential spin correlation ($e^{-\gamma t}$) for $\gamma \approx \hbar\omega_m = 0.5$ meV. For other values of γ this line has only to be shifted to the left or the right.

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