

## Direct Observation of Critical Phenomena by Incoherent Neutron Scattering

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(Received 22 July 1985)

The first direct spectral observation of critical *incoherent* quasielastic neutron scattering is reported. This result has been obtained by a combination of time-of-flight and high-resolution back-scattering spectrometers with use of a single crystal of selectively deuterated *p*-terphenyl in the vicinity of the order-disorder phase transition. The relation of the incoherent-scattering results to critical *coherent* neutron scattering is discussed.

PACS numbers: 64.60.Ht, 61.12.Ex, 64.60.Cn, 64.70.Kb

A number of magnetic-resonance studies have shown that collective critical fluctuations occurring near an order-disorder structural phase transition influence local dynamics.<sup>1</sup> These experiments gave evidence that the critical relaxational mode behavior (critical slowing down) significantly modifies the central part of the spectral density of the involved autocorrelation function. Quasielastic-incoherent-neutron-scattering spectra should also reflect these critical effects.<sup>2,3</sup> However, such an observation requires that the pretransitional fluctuations are important and appear in an accessible frequency range. Furthermore, the geometry of the molecular motion should be such that the quasielastic scattering, directly related to the structural phase transition, can be isolated. For all these reasons *p*-terphenyl (PTP) is a very suitable system. Indeed, the geometry of the molecular motion is particularly simple: Phenyl rings reorient by rotational "jumps" in a double-well potential corresponding to two equivalent nonplanar molecular conformations.<sup>4</sup> Moreover, the transition is continuous, or very close to continuous, and PTP is one of the rare molecular crystals where critical slowing down has directly been observed by coherent-neutron-scattering experiments.<sup>5</sup> In addition, NMR measurements have also shown a clear divergence of the spin-lattice relaxation rate  $T_1^{-1}$ .<sup>6,7</sup>

The incoherent-neutron-scattering function associated with the reorientational jumps of phenyl rings is

$$S_s(\mathbf{Q}, \omega) = A_0(\mathbf{Q})\delta(\omega) + [1 - A_0(\mathbf{Q})]S(\omega), \quad (1)$$

where  $A_0(\mathbf{Q})$  is the elastic incoherent structure factor (EISF). Well above the transition temperature, the single-molecular motion is well described by a random-disorder model. The quasielastic component

$S(\omega)$  has a Lorentzian shape whose width is twice the rate of exchange,  $1/\tau_R$ , between the two molecular conformations. On approaching  $T_c$ , we expect the shape of the quasielastic part to be modified by critical phenomena connected with the formation of short-range-ordered clusters. In fact a simple model based on a cluster-exchange reaction predicts the appearance in  $S(\omega)$  of a narrow quasielastic spectral component due to a cluster lifetime effect.<sup>3</sup> In previous work,<sup>8</sup> the measurement of this "critical" component in the incoherent-scattering function of fully hydrogenated powder ( $C_{18}H_{14}$ ) has only partially been successful because of its intrinsically low intensity and because high energy resolution is required. However, indirect evidence for its existence was obtained with the aid of "elastic"-energy-window measurements.<sup>8</sup> In the present paper we wish to report on the first direct spectral observation of the above-mentioned critical *incoherent* quasielastic scattering.

In order to make this experiment feasible, selectively deuterated powder and single-crystalline samples ( $C_6D_5$ - $C_6H_4$ - $C_6D_5$ ) were used. The partial deuteration appreciably reduces the elastic component of the incoherent-scattering function, since the largest amplitude of motion is that of the central ring. In the case of the  $C_{18}D_{10}H_4$  single crystal the elastic scattering is completely eliminated for particular scattering vectors (e.g.,  $\mathbf{Q}_0 \parallel \mathbf{a}^*$  with  $Q_0 = 3.76 \text{ \AA}^{-1}$ ). These arguments are illustrated in Fig. 1 by the plotting of the EISF<sup>9</sup> resulting from the dynamic conformational disorder for  $C_{18}H_{14}$  powder and for  $C_{18}D_{10}H_4$  powder as well as for the single-crystalline sample.

Incoherent-neutron-scattering measurements were made by means of two different instruments at the Institut Laue-Langevin in Grenoble: the time-of-flight

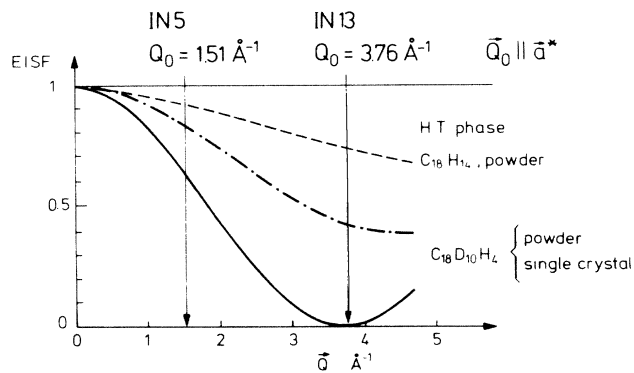


FIG. 1. Theoretical behavior of the EISF of *p*-terphenyl.

spectrometer IN5 [ $\lambda_0 = 6.167 \text{ \AA}$ ; energy resolution (FWHM)  $\Delta\hbar\omega \approx 80 \text{ \mu eV}$ ] and the backscattering spectrometer IN13 ( $\lambda_0 = 2.23 \text{ \AA}$ ;  $\Delta\hbar\omega \approx 7 \text{ \mu eV}$ ). The experimental conditions were such that coherent contributions to the scattered intensity were negligible both for the powder (see Ref. 8) and for the single crystal.

First we note that the IN5 measurements performed at  $T > 245 \text{ K}$ , i.e., far above  $T_c = 185.3 \text{ K}$ , nicely confirm the expected simple Lorentzian line shape. The integrated quasielastic intensity shows the  $Q$  dependence expected from the considered molecular motion. The exchange rate is found to follow a typical Arrhenius law,

$$\tau_R^{-1} = 2180 \exp[-(550 \text{ K})/T] \text{ \mu eV}, \quad (2)$$

similar to that observed in the case of  $C_{18}H_{14}$ .<sup>6,8</sup>

On IN13 we first made feasibility studies by measuring as a function of temperature the intensity of neutrons scattered into an energy interval (window) given by the experimental energy resolution. In Fig. 2 we show the results for the single-crystalline sample obtained with IN13 and energy windows centered (a) at  $\hbar\omega = 0$  and (b) at  $\hbar\omega = 12$  and  $24 \text{ \mu eV}$  (i.e., with  $\hbar\omega \ll 1/\tau_R$ ) at a mean elastic wave-vector transfer  $Q_0 = 3.76 \text{ \AA}^{-1}$  ( $Q_0 \parallel a^*$ ) corresponding to the theoretical minimum of the EISF (see Fig. 1). The "elastic"-window measurement [Fig. 2(a)] clearly shows the appearance of critical scattering on approaching the transition temperature. It verifies the value of the latter ( $T_c = 185.3 \text{ K}$ ) and qualitatively shows the effect of the increasing order parameter below  $T_c$ . In the "quasielastic"-window measurement ( $\hbar\omega > 0$ ) pronounced peaks are observed at  $T_c$  [Fig. 2(b)], suggesting that the central part of the quasielastic line is strongly increasing when the transition point is approached, and that critical scattering can be observed in a sizable temperature range around  $T_c$  with the given resolution. This result is direct phenomenological evidence of critical incoherent neutron scattering near the order-disorder phase transition of PTP.

Guided by the results from the window measure-

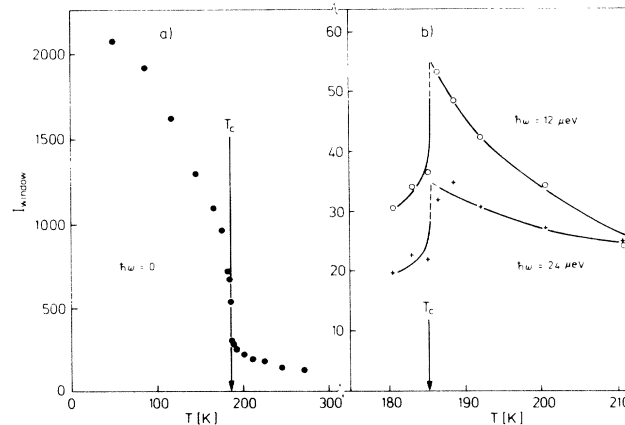


FIG. 2. (a) Elastic ( $\hbar\omega = 0$ ) window measurement and (b) quasielastic [ $\hbar\omega = 12 \text{ \mu eV}$  (circles) and  $\hbar\omega = 24 \text{ \mu eV}$  (crosses)] window measurements performed on a single crystal of  $C_{18}D_{10}H_4$  (at  $Q_0 = 3.76 \text{ \AA}^{-1}$ ,  $Q \parallel a^*$ ). Lines are guides for the eyes.

ments, we have recorded spectra using IN13 in the energy range of  $[-20, +100] \text{ \mu eV}$  at  $T_c + 1.1 \text{ K}$  and  $T_c + 6.9 \text{ K}$ , as well as far below ( $T = 43.5 \text{ K}$ ) and far above ( $T = 244.9 \text{ K}$ ) the transition temperature [Fig. 3(a)]. A powdered sample was also studied at the same temperatures on IN5, and the energy range of  $[-1000, +2000] \text{ \mu eV}$  was analyzed. The quasielastic part of the IN5 spectrum measured at  $Q_0 = 1.52 \text{ \AA}^{-1}$  at  $T_c + 6.9 \text{ K}$  is plotted in Fig. 3(b). The IN13 spectra taken at  $Q_0 = 3.76 \text{ \AA}^{-1}$  ( $Q_0 \parallel a^*$ ) clearly show the following features: At low temperature ( $43.5 \text{ K}$ ) an unbroadened resolution-shaped (elastic) peak is observed. At high temperature ( $244.9 \text{ K}$ ) the spectrum is composed of an elastic line and a very broad quasielastic component (appearing flat on the IN13 energy scale). However, on approaching  $T_c$  ( $192.2$  and  $186.4 \text{ K}$ ), a strong contribution to the central part of the quasielastic spectrum is seen to develop. Similar observations were made in a large  $Q$  range ( $1.3 \text{ \AA}^{-1} \leq Q \leq 4.3 \text{ \AA}^{-1}$ ) at about twenty different scattering angles, but—as expected from the EISF of the single crystal (Fig. 1)—in general with a weaker quasielastic intensity. The result confirms the quasielastic-window measurements and is the first spectral evidence of incoherent critical scattering.

In order to describe these quasielastic-incoherent-scattering data we have to introduce a model taking into account the occurrence of collective critical fluctuations. In previous work<sup>3</sup> a theoretical expression of  $S(\omega)$  was derived from a simplified model where only two characteristic times were introduced to describe the dispersion of the correlation times in the whole Brillouin zone:  $\tau_R$ , the above-defined (noncritical) correlation time for random reorientation in the double-well potential, and  $\tau_0$ , a cluster residence time averaged over the entire cluster distribution. Then the

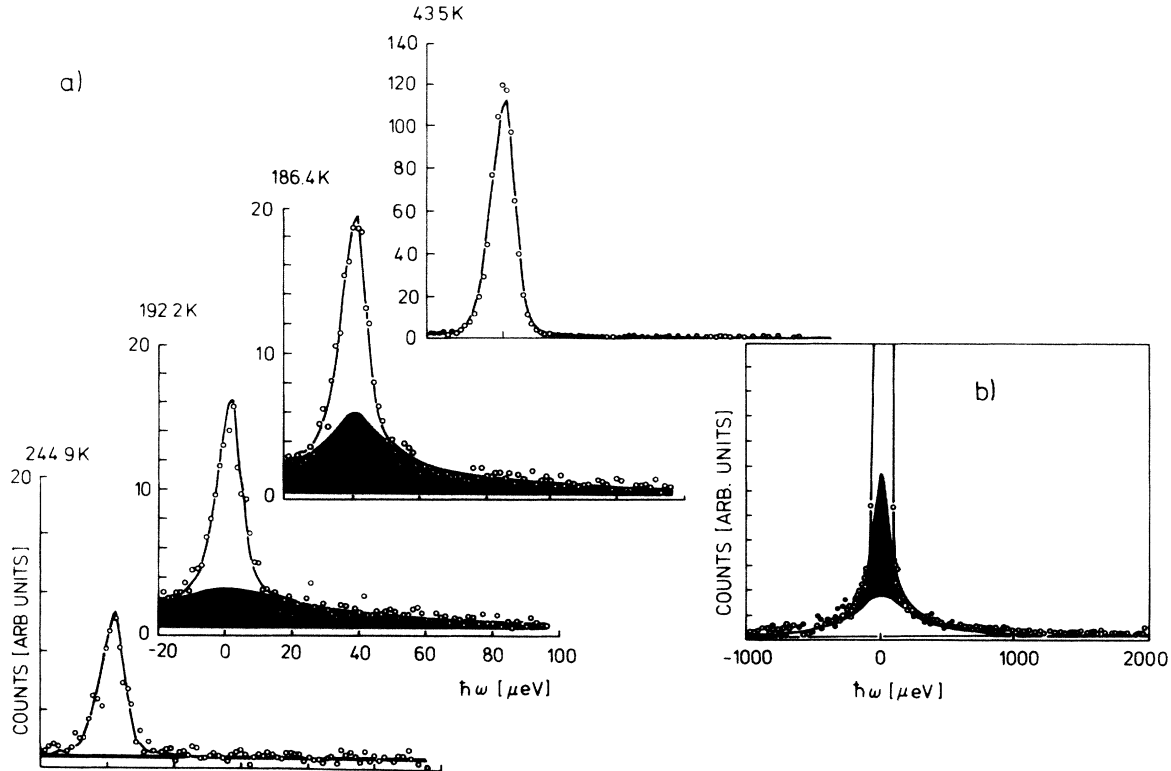


FIG. 3. Incoherent-neutron-scattering spectra obtained (a) with IN13 at ( $Q_0 = 3.76 \text{ \AA}^{-1}$ ,  $Q \parallel a^*$ ) from a single crystal of  $C_{18}D_{10}H_4$  and (b) with IN5 at  $Q_0 = 1.52 \text{ \AA}^{-1}$  from a powdered sample of  $C_{18}D_{10}H_4$ . Full lines are the results of a fit by our model. The critical component of the incoherent scattering function is shown in black.

quasielastic component splits into two contributions: one of critical origin, mainly governed by  $\tau_0$ , and the other, noncritical, governed by  $\tau_R$ :

$$S(\omega) = CS_{\text{crit}}(\omega) + (1 - C)S_{\text{noncrit}}(\omega), \quad (3)$$

The relative weight of the critical part is given by the parameter  $C$ .

Keeping this separation into critical and noncritical terms we will in the following introduce the wave-vector-dependent correlation times  $\tau_q$  associated with the Fourier components of the spatial fluctuations of the orientation. These are known from coherent neutron scattering on fully deuterated PTP<sup>5</sup> and are in good agreement with a mean-field approximation.<sup>10</sup> In order to simplify the calculation, we have considered isotropic collective fluctuations with a mean correlation length  $\xi$ . The dispersion relation reads

$$1/\tau_q = (1 + q^2\xi^2)/\tau_c. \quad (4)$$

Near  $T_c$ , for  $T > T_c$ , both the square of the correlation length  $\xi$  and the cluster lifetime  $\tau_c$  are found to behave approximately like  $(\Delta T)^{-1} = |T - T_c|^{-1.5, 11}$ . Thus, near  $T_c$  a strong dispersion of the correlation times  $\tau_q$  is expected from Eq. (4). This is confirmed qualitatively by the observation that the width of the coherent scattering for  $q=0$  at  $T_c + 1 \text{ K}$  is  $\tau_c^{-1} \approx 1$

$\mu\text{eV}$ , whereas at the same temperature Eq. (2) yields  $\tau_R^{-1} \approx 110 \mu\text{eV}$ . Here it must be noted that Eq. (4) is only valid for small wave vectors  $q$ ; for large vectors  $q$  the correlation times  $\tau_q$  have little dispersion and should approximately be equal to the single-molecule correlation time  $\tau_R$ . This justifies our phenomenological separation of  $S(\omega)$  according to Eq. (3).  $S_{\text{noncrit}}(\omega)$  is then again a simple Lorentzian with half width at half maximum of  $2/\tau_R$ , whereas  $S_{\text{crit}}(\omega)$ , the critical spectral contribution, is obtained by averaging of the coherent-quasielastic-scattering function

$$S(\mathbf{q}, \omega) = k_B T [1/(\xi^{-2} + q^2)] \tau_q^{-1} / (\tau_q^{-2} + \omega^2) \pi \quad (5)$$

over the critical region of the Brillouin zone:

$$S_{\text{crit}}(\omega) = \int_{\text{crit region}} S(\mathbf{q}, \omega) d^3q. \quad (6)$$

This has previously been calculated.<sup>12</sup> At  $T = T_c$ , this function diverges as  $\omega^{-1/2}$ . The critical region is defined by the reasonable (although somewhat arbitrary) requirement that the maximum value of  $\tau_q^{-1}$  is equal to  $\tau_R^{-1}$ .

Because of the various approximations made, the weight  $C$  of the critical scattering component is used as a parameter. Its value (0.41 at  $T_c + 6.9 \text{ K}$  and 0.57 at

$T_c + 1.1$  K) is at first extracted from a fit of the IN5 data and then used for describing the IN13 spectra. Note that these values are of course sensitive to the definition of the critical region. On IN13 a weak purely elastic contribution, observed above  $T_c$  and probably due to various small effects (such as multiple scattering), is described in the fit by the introduction of an extra elastic component. The resulting total scattering function convoluted with the resolution function describes both series of spectra very well. The results of these fits are shown in Fig. 3, the critical part being shown in black. The agreement is remarkable given that the same theoretical formula (with the same parameter values) is compared to data taken at rather different  $Q$  vectors, and in energy ranges and with energy resolutions both differing by an order of magnitude.

This direct experimental evidence of *critical-incoherent*-neutron scattering in PTP proves that this technique is an alternative method for the study of local critical dynamics. The window measurements presented are in a way analogous to NMR spin-lattice relaxation-rate measurements. However, incoherent neutron scattering in addition allows the measurement of the complete spectral density of the involved auto-correlation function. It should be possible to relate this spectral density to the correlation-time distribution of a generalized cluster-reaction theory.<sup>13</sup> Furthermore it may provide an estimation of the weight of critical fluctuations, a fundamental concept in the field of critical phenomena. It will be interesting to advance further in this direction in the future, as well as to look for similar phenomena in other compounds, where very large motional amplitudes of incoherently scattering atoms (especially hydrogen) occur in connection with critical fluctuations.

A full account of the incoherent-neutron-scattering results from PTP will be published later.

We are indebted to Professor R. Carrier and Dr. D. Gree for the preparation of the selectivity deuterated *p*-terphenyl. One of us (B.T.) would like to thank Professor H. Dachs and the Hahn-Meitner Institut for their hospitality while part of this work was performed.

Groupe de Physique Cristalline is unit  associ  au Centre National de la Recherche Scientifique 040804.

<sup>1</sup>F. J. Owens, C. P. Poole, and H. A. Farach, *Magnetic Resonance of Phase Transitions* (Academic, New York, 1979); A. Rigamonti, *Adv. Phys.* **33**, 115 (1984).

<sup>2</sup>K. H. Michel, *J. Chem. Phys.* **58**, 1143 (1973); T. Schneider and P. F. Meier, *Phys. Rev. B* **8**, 4422 (1973).

<sup>3</sup>R. E. Lechner, in *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese *et al.* (Plenum, New York, 1981), Vol. 2, pp. 441-448.

<sup>4</sup>J. L. Baudour, H. Cailleau, and W. B. Yelon, *Acta Crystallogr., Sect. B* **33**, 1773 (1977); H. Cailleau, J. L. Baudour, J. Meinel, A. Dworkin, F. Moussa, and C. M. E. Zeyen, *J. Chem. Soc. Faraday Trans. 1* **7**, 70 (1980).

<sup>5</sup>H. Cailleau, A. Heidemann, and C. M. E. Zeyen, *J. Phys. C* **12**, L411 (1979).

<sup>6</sup>B. Toudic, J. Gallier, P. Rivet, and H. Cailleau, *Solid State Commun.* **47**, 291 (1983).

<sup>7</sup>Z. Pajak, N. Pislewski, and J. Wasicki, in *Pulsed Nuclear Magnetic Resonance and Spin Dynamics*, edited by J. W. Hennell (Institute of Nuclear Physics, Krakow, Poland, 1978), p. 190; K. Kohda, N. Nakamura, and H. Chihara, *J. Phys. Soc. Jpn.* **51**, 3936 (1982); T. Gullion, M. S. Conradi, and A. Rigamonti, *Phys. Rev. B* **31**, 4388 (1985).

<sup>8</sup>R. E. Lechner, B. Toudic, and H. Cailleau, *J. Phys. C* **17**, 405 (1984); B. Toudic and R. E. Lechner, *J. Phys. C* **17**, 5503 (1984).

<sup>9</sup>For a detailed discussion of the EISF concept, see R. E. Lechner, in *Mass Transport in Solids*, edited by F. Beniere and C. R. A. Catlow (Plenum, New York, 1983), pp. 169-226; R. E. Lechner and C. Riekel, in *Neutron Scattering and Muon Spin Rotation*, edited by G. H hler and E. A. Niekisch, Springer Tracts in Modern Physics, Vol. 101 (Springer, Berlin, 1983).

<sup>10</sup>L. D. Landau and E. M. Lifshitz, *Physical Kinetics, Course of Theoretical Physics* (Pergamon, Oxford, 1981), Vol. 10.

<sup>11</sup>H. Cailleau, thesis, University of Rennes, 1981 (unpublished).

<sup>12</sup>R. Blinc, Z. Zumer, and G. Lahajnar, *Phys. Rev. B* **1**, 4456 (1970).

<sup>13</sup>K. Binder, D. Stauffer, and H. M ller-Krumbhaar, *Phys. Rev. B* **12**, 5261 (1975).

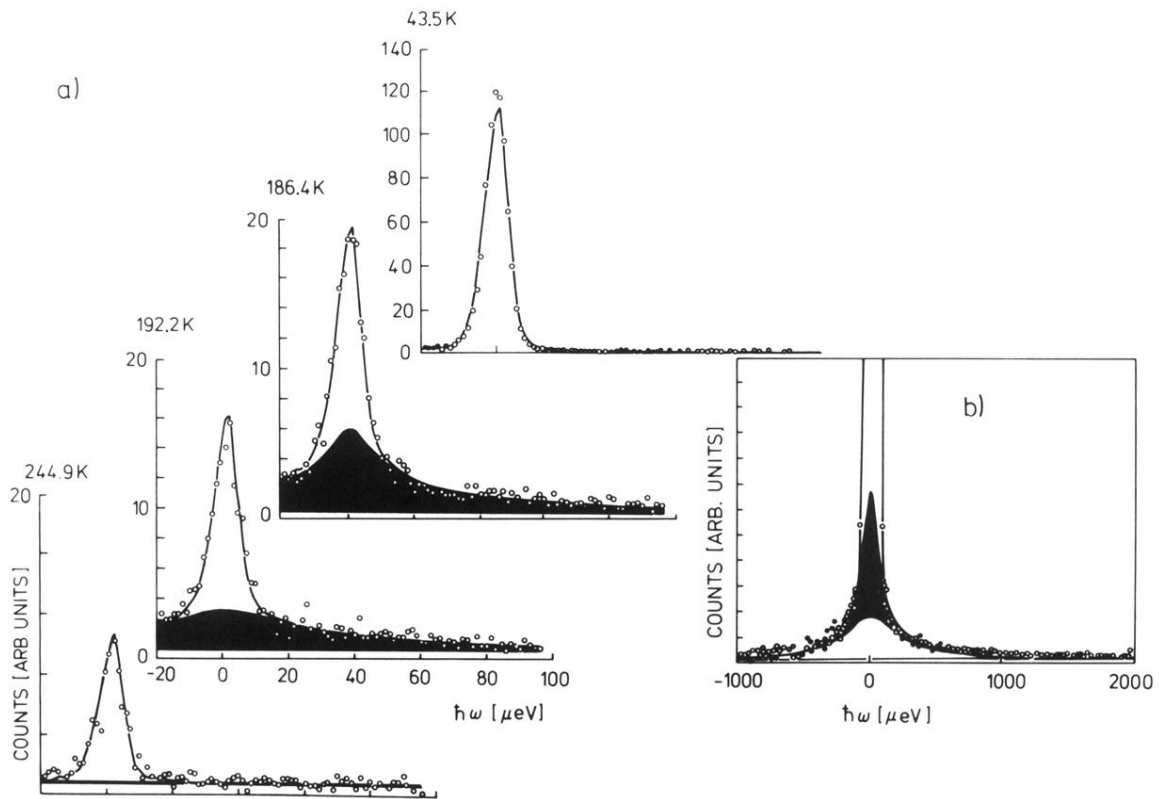


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