Neutron scattering in magnetic fields

W.C. Koehler

Revue Phys. Appl. **19** (1984) 691-695 SEPTEMBRE 1984, PAGE 691

Neutron scattering in magnetic fields (*)

W. C. Koehler

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, U.S.A.

Résumé. — On discute brièvement l'utilisation d'un champ magnétique dans certaines expériences de diffusion des neutrons. On distingue, en général, deux sortes d'applications. Pour l'une le champ agit pour changer les propriétés de l'échantillon ; pour la seconde, il interagit avec le neutron lui-même. On présente quelques exemples. On donne une revue des précautions à prendre pour obtenir des données très précises par la diffraction des neutrons polarisés.

Abstract. — The use of magnetic fields in neutron scattering experimentation is reviewed briefly. Two general areas of application can be distinguished. In one the field acts to change the properties of the scattering sample ; in the second the field acts on the neutron itself. Several examples are discussed. Precautions necessary for high precision polarized beam measurements are reviewed.

1. Introduction.

The uses of magnetic fields in neutron scattering experiments can be divided into two, not necessarily mutually exclusive, areas. In one, a field is applied to modify the properties of the scattering sample. This modification may manifest itself in a variety of ways. In magnetic structure studies it is sometimes possible to produce single-domain specimens, the preparation of single-Q crystals of chromium by field-cooling is a good example [1, 2]. A large body of research has utilized the directional sensitivity of the scattering of neutrons by electronic magnetic moments. Since only those components of the moments that are perpendicular to the scattering vector participate in the scattering process, the magnetic scattering can be made to go to zero, or to a maximum by turning the moments into or perpendicular to the scattering vector. An example is the separation of magnetic diffuse scattering from nuclear diffuse scattering in ferromagnetic 3-d alloys. This directional dependence is as well the basis for the ORNL magnetically-pulsed correlation chopper [3]. Strong magnetic fields are used to induce magnetic moments in paramagnetic metals and these are in turn investigated with polarized beams produced by the action of a magnetic field on a suitably tailored monochromator-polarizer. Moderate to strong fields are used to induce magnetic phase transitions and to investigate the related areas of multicritical phenomena and more recently, the random field problem. In the area of inelastic scattering the application of a magnetic field can alter the magnon spectrum. The study of magnon dispersion in applied fields has been used to isolate the sources of anisotropy in rare earth metals.

At very low temperatures and in strong magnetic fields systems of nuclear moments can become polarized to an appreciable extent. This can have important consequences in neutron crystallography [4], in the measurement of spin dependent scattering lengths of appropriate nuclei [5], and in the observation of order in nuclear spin systems.

With the advent of pulsed neutron sources one may anticipate that pulsed magnets will be used to achieve very high fields and make possible the investigation of transient magnetic behaviour on a microscopic scale. With these sources have come intensified efforts to develop new methods of polarizing thermal and epithermal neutron beams. For the steady state source the energy of the incident neutron beam is usually well defined. The polarizer (crystal, mirror, multilayer) need function at but a single wavelength at a time. With a pulsed neutron source one has need to polarize a « white » beam. Methods under consideration at present involve brute force polarization of protons in very high fields and very low temperatures and the dynamic polarization of protons, in relatively

(*) Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

high fields and low temperatures, by coupling the proton spins with those of a paramagnetic impurity in a neutron filter [6, 7].

My second broad category is one in which a field or fields interact primarily with the magnetic moment of the neutron, and those may be applied independently of the field on the sample. Examples of applications in this category are not limited to magnetic systems. The whole catalogue of experiments performed with polarization analysis (spin spectroscopy), neutron spin echo and flipper-chopper techniques [8] can be cited.

2. Experimental results.

In what follows I will select a few examples to discuss in greater detail. The choice is based on my own interests and, primarily on work carried out at the Oak Ridge National Laboratory. In keeping with the theme of this workshop I have tried, wherever it is indicated, to include some technical aspects of the application of magnetic fields to samples in scattering experiments. You will be able to find, of course, many other and equally interesting examples.

3. Paramagnetic transition metals.

Let me begin with a discussion of the measurement of the magnetic form factors of paramagnetic transition metals. The experimental situation was reviewed, in this room, in October of 1982, by R. M. Moon [9] during an International Conference on the Impact of Polarized Neutrons on Solid-State Chemistry and Physics. A little earlier, in May 1982, I presented a survey of magnetization densities in solids, also in this room, at a Conference on the Densities of Electrons in Solids, organized in honor of E. F. Bertaut. I think it fair to say that since then little new has been added to the experimental literature for paramagnetic metals. Considerable progress has been made in the theory, however, the most recent review having been given by Harmon [10] at the International Conference mentioned above, and I will cite the results of recent calculations being carried out at the Laboratory.

The experiments have been made possible by the addition of superconducting magnets to polarized-beam diffractometers ; one studies the induced moment form factor. The field is applied to a single crystal sample in a direction normal to the scattering vector for a Bragg reflection and then the peak intensity is measured for neutrons polarized parallel and anti-parallel to the field on the sample. Generally the magnitudes of the induced moments are small, of the order of a few milli-Bohr magnetons so that the ratio of the measured intensities, the flipping ration R, can be expressed as

$$R = 1 + 4\,p(\tau)/b\,; \quad r = R - 1 = 4\,p(\tau)/b \qquad (1)$$

where r is the residual flipping ratio, b the nuclear scattering amplitude and $p(\tau)$ the q dependent magnetic scattering amplitude measured at reciprocal lattice vectors.

Contained in $p(\tau)$ is the Fourier transform of the electronic magnetization, and this can be related to the zz component of the generalized static susceptibility, evaluated at reciprocal lattice points. From the flipping ratio experiments we obtain, then, values of

$$\chi^{zz}(\tau, 0) = \chi_{sp}(\tau) + \chi_{orb}(\tau) - (\chi_{dia}^{core}(\tau) + \chi_{dia}^{Lan}(\tau)) \qquad (2)$$

where the first term is the contribution of Pauli spin paramagnetism, the second, Van Vleck orbital paramagnetism and the third and fourth the diamagnetic contributions from the core and outer electrons respectively. It is usual to subtract off the third term, using an expression due to Stassis [11], leaving a susceptibility due only to the outer electrons, χ_0^{zz}.

There are a number of difficulties associated with deriving accurate values of $\chi_0^{zz}(\tau)$ from the experiments. Long counting times are required and this sets stringent demands on the stability of the system. In addition, there are such effects as nuclear polarization, the neutron-spin neutron-orbit interaction, diamagnetic scattering, sample purity, and extinction that must be eliminated or for which corrections must be made. In general, these corrections can be made, reliably, but there is a class of errors inherent in the experimental arrangement employed that set a lower limit on the ultimate accuracy that can be achieved. These have been discussed in two earlier papers [12, 13] but I should like to mention the most important again here.

Let us first look quickly at the levels of uncertainty that we are considering. If we rewrite equation (1) for the residual flipping ratio, expressing the atomic susceptibility in emu/mol, the applied field in Oe and b in 10^{-12} cm, we obtain

$$r = 1.93 \times 10^{-4}\,\chi H f(\tau)/b\,. \qquad (3)$$

In a favorable case with $\chi = 10^{-3}$, $H = 6 \times 10^4$, $b = 0.5$, one finds $r = 0.23\,f$ and if we are asking to measure f to say $\pm$ 0.025 then $\Delta r = 6 \times 10^{-4}$ or we are asking to measure R with an uncertainty of about 5×10^{-4}. Generally we will be interested in experiments in which we want accuracies in the flipping ratios in the range 5×10^{-5} to 5×10^{-4}.

In most discussions of the polarized-beam technique, it is implicitly assumed that there is no change in the velocity distribution of the incident neutrons when their spin is reversed. This is not really true because as the neutrons enter the magnetic field at the sample position they are subject to a force produced by the magnetic field gradient of the sample magnet and the direction of this force is opposite for the two spin states. This produces different velocity and position distributions for the two spin states at the sample location and affects the observed flipping ratio. The most important of such effects is the change of velocity,

or of wavelength resulting in a different Bragg angle, about 10^{-4} deg, for the two spin states. As shown in reference [12], the error in the flipping ratio is given by

$$\Delta R = -\frac{2\,|\mu_n|}{m_n V_0^2} \tan\theta H \frac{1}{S(\theta)} \frac{dS(\theta)}{d\theta}. \qquad (4)$$

Where μ_n is the neutron moment, V_0 the neutron velocity, H the central field and $S(\theta)$ describes the shape of the rocking curve. It is important to position the crystal so that $dS(\theta)/d\theta$ is as nearly zero as possible. In the earlier work we pointed out that a deviation of as little as 0.02 deg can produce effects far in excess of the desired total error of about 10^{-4} especially for sharp rocking curves. The ideal crystal for measurements of this type has a broad, flat-topped rocking curve.

There is another adverse effect that is peculiar to the superconducting magnets constructed for polarized beam work. These are usually built with unequal turns in the upper and lower coils, an asymmetric split-coil, in order to move zero-field regions of the fringe field out of the neutron beam path and thus avoid beam depolarizing effects. This has the undesirable side-effect that there is a vertical field gradient all along the neutron flight path and this gradient produces a vertical separation of the two neutron spin states. The vertical angular deviation between two neutrons with opposite spins, each initially travelling on the same horizontal path with equal velocities is

$$\delta(\uparrow) - \delta(\downarrow) = -\frac{2\,\mu_n}{m_n V_0^2} \int \frac{\partial H}{\partial z}\, d\rho \qquad (5)$$

where the integration is along the neutron path both into and out of the magnet. For the Oak Ridge magnet [14] operated at 60 kOe this angular deviation is about 6×10^{-4} deg resulting in a vertical separation at the counter of about 10^{-3} cm. Ordinarily this is not a problem. However, if the crystal is slightly misaligned so that the reciprocal lattice vector is not exactly in the horizontal plane, the observed intensity can be sensitive to the vertical divergence with a resulting error in the flipping ratio. Errors of 10×10^{-4} can easily result.

Thus these field effects can produce very serious errors in polarized beam measurements. With reasonable caution reliable results can be obtained to accuracies in the flipping ratios of about 10^{-4} but this is probably approaching the limit of the technique as presently practiced. As Moon [9] has shown in his graphical construction, these errors preclude the study of those metals with very low susceptibilities. Most of the metals capable of being studied experimentally have already been studied and further progress will come from refinements and advances in methods of interpretation of the existing data.

The task of calculating all the contributions to $\chi^{zz}(\mathbf{q}, 0)$ is a difficult one, and up to now, a relatively complete calculation has been made only in the case of Cr by Oh *et al.* [15]. In all other cases the data have either been interpreted with free atom form factors with an appropriate mix of spin and orbital contributions as determined from other types of experiments, or with spin form factors based on APW calculations. The expansion expected for electron wave functions near the bottom of the d-band and observed in Sc [16], and Lu [17] was in fact strikingly reproduced in APW [17, 18] calculations of the spin-only form factor. The agreement is in fact too good since it leaves little room for an expected orbital contribution. Recently Cooke, Liu, and Liu, in the Theory Group of the ORNL Solid State Division have developed elegant computational techniques in order to extend the calculations of $\chi^{zz}(\mathbf{q}, 0)$ to all the pertinent paramagnetic metals. At present they have repeated the calculation for Cr, obtaining identical results with much less computer time than previously and have new results for the bcc metals V, Nb, and Mo. It is anticipated that results for fcc and hcp metals will be forthcoming in the next few months. Figure 1 shows the experimental results for Nb as reported in Moon, Koehler, and Cable [13], and the calculated form factor [19]. With these new calculations one may hope to fully exploit the experimental capabilities of polarized beam diffractometry for investigations of electronic wave functions in the solid.

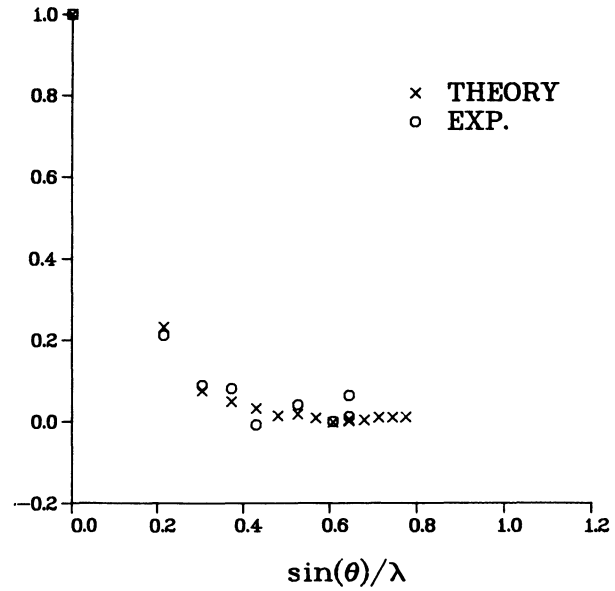

Fig. 1. — Experimental and theoretical form factors for niobium. The calculation includes both orbital and spin contributions. A spin enhancement factor was obtained from a fit to the experimental g factor. The free atom form factor for Nb falls off much less rapidly.

4. Structure and Lifshitz behaviour of MnP.

Manganese phosphide is ferromagnetic below $T_c = 291$ K and antiferromagnetic below 50 K [20].

Neutron diffraction measurements by Forsyth, Pickart and Brown [21] and by Felcher [22] showed that the antiferromagnetic phase was a spiral. Until recently there have been some questions as to the details of the spiral structure.

MnP has an orthorhombic crystal structure with strong magnetic anisotropy. Choosing axes $a > b > c$ the easy axis is along c and the hard axis along a. In the spiral phase the propagation vector is parallel to a and the moment rotates in the bc plane. The structure is in fact a double spiral ; sheets of manganese spins are separated alternately by 0.1 a and 0.4 a. Spins in the sheets widely separated are parallel. Spins in the closely separated sheets make an angle with each other. Application of a field along the b-direction at temperatures below about 121 K produces a transformation to an oscillatory phase, a fan structure in which the moments in the bc planes rock about the field direction in a periodic fashion with a wave vector $\mathbf{q} = 2\pi/a\ \delta a$.

The questions concerning the helical phase have to do with the relative magnitudes of the c- and b-components of the spiral. Is one dealing with an elliptical spiral where the two are of different magnitude, or a circular spiral where they are equal ? If the magnitudes of orthogonal components are equal, can the moments be bunched to a greater or lesser degree around the easy direction as suggested by Hiyamizu and Nagamiya [23]?

With the neutron polarization analysis technique [24] it is a simple matter to measure the relative magnitudes of orthogonal moment components by observing just a single magnetic satellite. One measures separately the spin-flip $(-+)$ and spin-non-flip $(++)$ cross sections. The latter comes from moment components parallel to the neutron polarization and the former from those perpendicular to it. Such an experiment, involving the $(2 \pm \delta, 0, 0)$ satellites has been carried out by Moon [25]. He finds a ratio R of $(-+)/(++)$ at 4.3 K equal to 1.091 ± 0.007. A circular helix with no distortions would produce equal $(-+)$ and $(++)$ intensities so that a more complex model is indicated. For an elliptical helix the measured ratio would simply be $(\mu_c/\mu_b)^2$ and further there should be only first order satellites. In the bunched-moment model $R = \left(\frac{1+\xi}{1-\xi}\right)^2$ where ξ is a bunching parameter : moreover the bunching distortion will produce third order satellites. These were expected to be very weak, of the order of 5×10^{-4} as intense as the first order satellites, but, knowing where to look, Moon was able to find and to measure them. The conclusion is that the bunching model of Hiyamizu and Nagamiya is correct with a value for the bunching parameter $\xi = 0.0218 \pm 0.0018$. In the above experiments the sample was mounted in the gap of the superconducting solenoid so that b was parallel to the small vertical field necessary to maintain the neutron polarization. The results were independent of field up to 0.6 T.

The same material was investigated at higher temperatures and fields to study possible Lifshitz behaviour. Many theoretical investigations of the Lifshitz point (LP) have been carried out in recent years [26] but there has been no direct experimental evidence on its existence. In a magnetic system the LP is a tricritical point at which three phases coexist. Recently, Becerra *et al.* [27] from a phase diagram deduced from magnetostriction measurements and from susceptibility data concluded that the para-ferro-fan triple point at about 121 K is a LP. The LP system has very special properties. The fan phase must have an oscillatory wave vector that is a function of field and temperature and that approaches zero continuously as the LP is approached. The transitions from the paramagnetic to both ordered states are of second order and certain special critical properties are predicted. Neither set of the measurements [27] gave direct evidence on the variation of q in the fan phase. Neutron diffraction measurements [28] made as a function of H (along b) and T, in the superconducting solenoid on MnP do support the conclusion that the triple point at 121 K is a LP.

The basic experiment consists of a longitudinal, elastic scan through the (200) position. At a given temperature a field was chosen, based on the phase diagram of reference [27] that was slightly below the ferro-fan boundary. With the temperature fixed the scan was repeated as the field was increased in steps until the magnetic satellites were no longer visible. It is difficult to make measurements of the satellites as T gets very close to T_L but the data show that q decreases continuously along the para-fan boundary as the triple point is approached, extrapolating to zero at a temperature close to that obtained from other

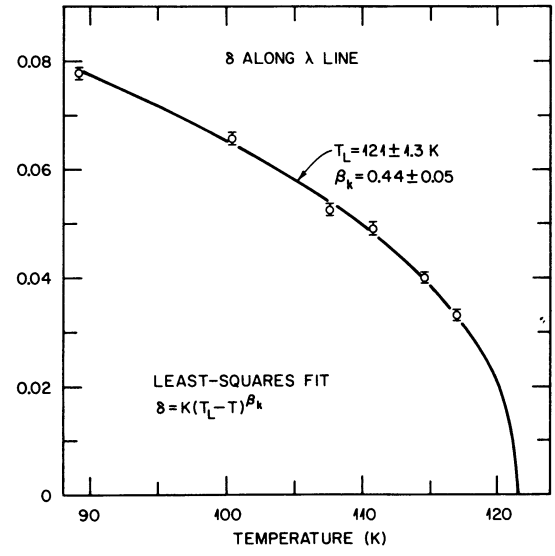

Fig. 2. — Temperature dependence of δ along the fan-para phase boundary in MnP. The solid line is a least squares fit of the theoretical relation to the experimental data.

determinations of the triple point. Figure 2 is a summary of the variation of δ along the fan-para phase boundary. The temperature dependence is in approximate agreement with the theoretical prediction of a LP.

This is clearly just one example of many where the application of an external field to a scattering sample is used in the study of phase transitions and critical phenomena.

I will conclude with remarks, en passant, on two additional problems. These certainly merit more space than I can give them here and I refer the reader to the original literature. There has been great interest in the existence and of the magnitude of anisotropic two-ion exchange in the heavy rare earth metals [29]. An assessment of this anisotropy energy is accessible from the spin wave spectra of Er in the conical phase, [30] and from a study of the spin wave spectra of the ferromagnets Tb [31] and Dy [32] in an applied magnetic field. Additional anisotropy information can be derived from the (H, T) dependence of the spin wave energy gap at $q \approx 0$. In these experiments a field of 40-60 kOe (higher fields would be useful) is applied to the specimen along the easy, and the hard, directions in the base plane. Care must be taken to prevent the strong torques that develop when the field is along the hard direction from twisting the sample in its mount.

Finally, as part of a co-operative program between the United States and Japan there has been initiated at Oak Ridge a program for neutron scattering at very low temperatures. Among the first such studies is that of the hyperfine-enhanced nuclear spin order of $HoVO_4$ [33]. In these experiments the sample is cooled in zero field, below about 30 mK in a dilution refrigerator. Then starting from about 3 T the crystal is cooled by self-demagnetization to 2.7 mK. Below 4.5 mK, magnetic diffraction peaks due to antiferromagnetic order in the hyperfine-enhanced spin system were observed.

References

[1] BASTON, T. J. and STREET, R., *Proc. Phys. Soc.* **86** (1965) 1143.

[2] WERNER, S. A., ARROTT, A. and KENDRICK, H., *J. Appl. Phys.* **37** (1966) 1260.

[3] MOOK, H. A., SNODGRASS, F. W. and BATES, D. D., *Nucl. Instrum. Methods* **16** (1974) 205.

[4] HAYTER, J. B., JENKIN, G. T. and WHITE, J. W., *Phys. Rev. Lett.* **33** (1974) 696.

[5] ABRAGAM, A., BACCHELLA, G. L., COUSTHAM, J., GLATTLI, H., FOURMOND, M., MALINOVSKI, A., MERIEL, P., PINOT, M. and ROUBEAU, P., *J. Physique Colloq.* **43** (1982) C7-373.

[6] ABRAGAM, A. and GOLDMAN, M., *Rep. Progr. Phys.* **41** (1978) 395.

[7] FELCHER, G. P., KLEB, R., HINKS, D. G. and POTTER, W. H., *Phys. Rev.* in press.

[8] See for example the Proceedings of the Institut Laue-Langevin Workshop on Neutron Spin Echo *Lecture Notes in Physics* **128** (Springer-Verlag) 1980. F. Mezei ed., and Proceedings of the International Conference on the Impact of Polarized Neutrons on Solid-State Chemistry and Physics, *J. Physique Colloq.* **43** (1982) C7.

[9] MOON, R. M., *J. Physique Colloq.* **43** (1982) C7-187.

[10] HARMON, B. N., *J. Physique Colloq.* **43** (1982) C7-177.

[11] STASSIS, C., *Phys. Rev. Lett.* **24** (1970) 1415.

[12] MOON, R. M., KOEHLER, W. C. and SHULL, C. G., *Nucl. Instrum. Methods* **129** (1975) 151.

[13] MOON, R. M., KOEHLER, W. C. and CABLE, J. W., Proc. Conf. on Neutron Scattering, Gatlinburg, 1976 (Conf-760601-P2) p. 577.

[14] An asymmetric split-coil solenoid with a 3/4 gap, 60 kOe maximum field, manufactured by Oxford Instruments.

[15] OH, K. H., HARMON, B. N., LIU, S. H. and SINHA, S. K., *Phys. Rev. B* **14** (1976) 1283.

[16] KOEHLER, W. C. and MOON, R. M., *Phys. Rev. Lett.* **36** (1976) 616.

[17] STASSIS, C., KLINE, G. R., LOONG, C.-K. and HARMON, B. R., *Solid State Commun.* **23** (1977) 159.

[18] GUPTA, R. P. and FREEMAN, A. J., *Phys. Rev. Lett.* **36** (1976) 613.

[19] COOKE, J. F., LIU, S. H. and LIU, A., private communication.

[20] HUBER, E. E. and RIDGLEY, D. H., *Phys. Rev. A* **135** (1964) 1033.

[21] FORSYTH, J. B., PICKART, S. J. and BROWN, P. J., *Proc. Phys. Soc.* **88** (1966) 333.

[22] FELCHER, G. P., *J. Appl. Phys.* **37** (1966) 1056.

[23] HIYAMIZU, S. and NAGAMIYA, T., *Int. J. Magn.* **2** (1972) 33.

[24] MOON, R. M., RISTE, T. and KOEHLER, W. C., *Phys. Rev.* **181** (1969) 920.

[25] MOON, R. M., *J. Appl. Phys.* **53** (1982) 1956.

[26] For a recent review see HORNREICH, R. M., *J. Magn. Magn. Mater.* **15-18** (1980) 387.

[27] BECERRA, C. C., SHAPIRA, Y., OLIVEIRA, N. F., Jr. and CHANG, T. S., *Phys. Rev. Lett.* **44** (1980) 1692.

[28] MOON, R. M., CABLE, J. W. and SHAPIRA, Y., *J. Appl. Phys.* **52** (1981) 2025.

[29] See for instance LINDGARD, P.-A., *Phys. Rev. B* **17** (1978) 2348 and references therein.

[30] NICKLOW, R. M., WAKABAYSHI, N., WILKINSON, M. K. and REED, R. E., *Phys. Rev. Lett.* **27** (1971) 334.

[31] See the series of papers by JENSEN, HOUMANN, BJERRUM-MØLLER and TOUBORG, *Phys. Rev.* **12** (1975) 303, 320 and 332.

[32] NICKLOW, R. M., KOEHLER, W. C. and NIELSEN, M., ORNL Solid State Division Annual Progress Report, ORNL 4952 (1973) p. 114 and NICKLOW, R. M. and KOEHLER, W. C., ORNL Solid State Division Annual Progress Report, ORNL 5028 (1974) p. 84.

[33] SUZUKI, H., OHTSUKA, T., KAWARAZAKI, S., KUNITOMI, N., MOON, R. M. and NICKLOW, R. M., *Solid State Commun.* 1984 in press.