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Magnetic effects on the symmetry of CBED patterns of ferromagnetic $PrCo_5$

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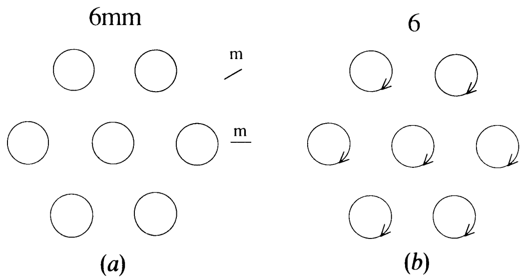
ABSTRACT

A high-energy permanent magnet, whose non-magnetic structure belongs to the space group $P\frac{6}{m}mm$, has been used to study the magnetic effect on symmetry determination by convergent-beam electron diffraction (CBED) patterns. At the [0001] zone axis, along which the magnetization of the domains is aligned, the symmetry of CBED patterns remains 6mm as if the specimen were non-magnetic. However, at the $[11\bar{2}0]$ zone axis, the mirror planes contained by the *c* axis were absent in the zero-order disks even though the whole pattern appeared to have 2mm symmetry. By looking into the interaction between the electron beam and the magnetic field produced by the specimen, it was found that the magnetic effect of the specimen was zero in the first-order approximation when the electron beam was along the [0001] direction, and was maximized when the electron beam was parallel to the basal plane. The apparent 2mm symmetry in the whole pattern of $[11\bar{2}0]$ zone axis indicates that diffraction is overwhelmed by the Coulombic potential in the specimen.

It is well known that the symmetry of crystals which are periodic in three dimensions can be described by one of 230 distinct space groups. These space groups describe all possible combinations of reflections, inversions and rotations that are consistent with three-dimensional translational symmetry. Determination of the point group symmetry by means of convergent-beam electron diffraction (CBED) has been systematically discussed by Buxton, Eades, Steeds and Rackham (1976). They established connections between the 32 crystal point groups and the 31 possible diffraction groups of CBED patterns. Later works discussed how to determine the space group by considering dynamic extinction present in CBED patterns (Gjønnes and Moodie 1965, Tanaka, Sekii and Nagaswa 1983). The CBED technique has been widely used in determining the symmetry group of many materials (Kaufman and Fraser 1985). In all of these works, the symmetry that is discussed is the symmetry of the Coulombic field that surrounds the atoms which make up the crystal that is being investigated.

In magnetic materials another type of symmetry is important, namely that of the total spin of magnetic ions in the crystal. Including the total spin of the magnetic ions differentiates them from each other. In the simplest case where the total spin J is $\frac{1}{2}$, there are two types of ions: namely spin up and spin down. This means that ions with the same number of electrons, protons and neutrons can be distinguished by the projections of their total spins. Thus an additional set of symmetry elements is necessary to specify the complete symmetry of magnetic materials. This symmetry is sometimes called 'black and white' symmetry, which is a subset of colour symmetry (Shubnikov 1960, Shubnikov and Belov 1964).

Fig. 1



(a) A projection of the point group $\frac{6}{m}$mm showing two of the associated vertical mirror planes. (b) The point group loses its vertical mirror planes on ferromagnetic ordering, becoming $\frac{6}{m}$.

We will not go into the details of colour symmetry in this Letter. One aspect will be discussed, however, namely the loss of vertical mirror planes in uniaxial magnetic materials. To illustrate this point, let us consider fig. 1, which displays the projection of the point groups $\frac{6}{m}$mm and $\frac{6}{m}$. If the atoms have the identical total spins which are aligned as shown in fig. 1 (b), it can be seen that there can be no vertical mirror planes. Thus a crystal with space group symmetry P$\frac{6}{m}$mm loses the mirror planes parallel to the sixfold axis upon ferromagnetic ordering along that axis. The space group symmetry therefore becomes P$\frac{6}{m}$. Note that the mirror plane perpendicular to the sixfold axis of rotation is not lost upon ferromagnetic ordering along that axis.

It is of course one thing for a crystal to have a certain symmetry but another thing to be able to detect it. Also, the diffraction techniques may not be sensitive to the specific changes in symmetry that are being studied. For example the conventional diffraction techniques may not be able to detect the absence of a centre of inversion (Friedel's law).

To ensure that the magnetic symmetry of a material can be investigated, the following properties of the material are necessary. First, the ferromagnetic material must have a large magnetic moment, since, in general, the magnetic interaction is much weaker in solids than the electronic Coulomb interaction. Second, the domain size of the ferromagnetic specimen must be much greater than the beam size of the electrons used in the technique. If this were not the case, the various domains would yield an averaged symmetry. Finally, the domains should extend through the thin region of the foil being investigated. Hence materials should have a simple domain structure.

The compound $PrCo_5$ belongs to the space group P$\frac{6}{m}$mm (Wernick and Geller 1959) and has uniaxial magnetic anisotropy. In consequence, it has the simplest domain structure, consisting of antiparallel domains separated by 180° domain walls. Its calculated magnetic moment (9·9 μ_B) is even higher than that of the compound $SmCo_5$ (7·8 μ_B), which is one of the two most widely used high-energy permanent magnets. The estimated domain size is about 0·5 μm (Shen, Laughlin, Velu and Sankar 1989) which is significantly larger than the beam size used in CBED technique (500 Å). All these properties of the $PrCo_5$ compound render it an ideal candidate to study the magnetic effect on the symmetry determination using the CBED technique.

The material used in the study was in the form of a sintered magnet fabricated from commercial grade Pr and Co near the stoichiometric $PrCo_5$ composition. The magnet had an intrinsic coercivity $H_{ci} = 2400$ Oe, a remanent induction $B_r = 9630$ G, and an energy product $(BH)_{max} = 17{\cdot}5$ MG Oe. The estimated domain wall thickness is about 65 Å. The magnet was in the shape of a cylinder 1 cm long and 0·42 cm in diameter. It was demagnetized by thermal annealing at a temperature slightly above the Curie temperature (912 K) for 10 min before being sliced both perpendicular to and parallel to the magnetization direction (*c* axis). Thin specimens were prepared by ion-milling, and were subsequently examined with a Philips 420T microscope operated at 120 kV. CBED studies were carried out in a double-tilt cold-stage holder cooled to 155 K and with a beam size of 500 Å.

TEM studies showed that the specimen consisted mainly of the $PrCo_5$ phase. A small amount of minor phases, such as Pr_2O_3 and $PrCo_2$ particles, were found in the sample. The $PrCo_5$ grains of 5 to 10 μm in diameter were almost defect-free. The grains were well aligned with their hexagonal *c* axis along the magnetization direction. No structural defects or strain contrast were observed in the regions where CBED patterns were taken.

A magnetic moment can be represented as an *axial* vector, and therefore has the symmetry of the Curie limiting group $\frac{\infty}{m}$ (Shuvalov 1988). When this symmetry is intersected with the point group $\frac{6}{m}$mm, with the moment parallel to the *c* axis, the resulting point group is given by

$$\frac{6}{m}\mathrm{mm} \cap \frac{\infty}{m} = \frac{6}{m}.$$

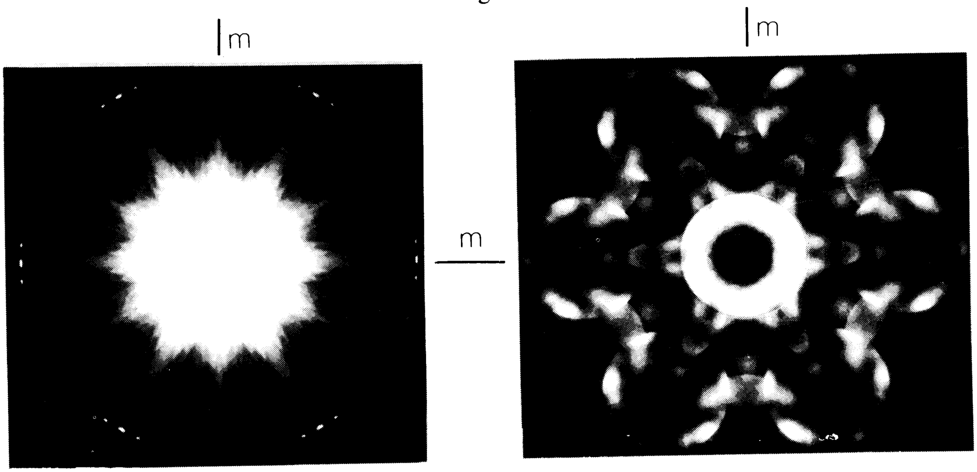
As can be seen from fig. 1, a crystal with the space group $P\frac{6}{m}$mm loses its vertical mirror planes upon ferromagnetic ordering. Thus a single magnetic domain of the ferromagnetic $PrCo_5$ compound has the symmetry $\frac{6}{m}$. The table shows relevant data about the point groups $\frac{6}{m}$mm and $\frac{6}{m}$ (Loretto 1984). From the table, it is clear that we could differentiate these two symmetry groups by examining the CBED patterns of the [0001] and [$11\bar{2}0$] zone axes. Because the magnetization of the domain is along the [0001] direction, the magnetic induction due to the magnetization has a zero component perpendicular to the incident beam when the electron beam is along the [0001] zone axis. It has a maximum perpendicular component when the electron beam is along the [$11\bar{2}0$] zone axis. It should be kept in mind that it is the perpendicular component of the magnetic induction that gives rise to the Lorentz force on the incident electrons. Thus, by examining the CBED patterns of zone axes both parallel and perpendicular to the *c* axis, we are able to explore the effect of the specimen's magnetization on the symmetry determination by the CBED technique.

As is shown in the table, both the zero layer symmetry and whole pattern symmetry of [0001] zone axis should have symmetry 6 for the space group $P\frac{6}{m}$. Surprisingly, the observed symmetry in both the zero-layer pattern and the whole pattern of [0001] is 6mm (figs. 2 (*a*) and (*b*)). At the [$11\bar{2}0$] zone axis, however, the mirror symmetry from the mirror planes parallel to the *c* axis was found to be absent in the zero-layer disks even

Symmetry of CBED patterns for point group $\frac{6}{m}$mm and $\frac{6}{m}$. The $11\bar{2}0$ and $1\bar{1}00$ directions are not twofold axes.

Point group	Zone axis	Diffraction group	Symmetry of whole pattern	Symmetry of zero-layer disks
$\frac{6}{m}$mm	0001	$6mm1_R$	6mm	6mm
	$11\bar{2}0$	$2mm1_R$	2mm	2mm
	$1\bar{1}00$	$2mm1_R$	2mm	2mm
$\frac{6}{m}$	0001	61_R	6	6

Fig. 2



(*a*) (*b*)

(*a*) The whole patterns of [0001] zone axes; and (*b*) the corresponding zero-layer disks.

though the whole patterns still appear to have distinctive 2mm symmetry (fig. 3). It is worth pointing out that the mirror symmetry from the mirror plane perpendicular to the *c* axis was retained in the zero-order disks of the $[11\bar{2}0]$ ĈBED pattern in fig. 3.

In order to understand these results better, let us look into the interaction between an electron beam and a magnetic specimen. The Hamiltonian of the system can be written as

$$H=\frac{h^2k^2}{2m}+H', \tag{1}$$

$$H'=U(\mathbf{r})+\frac{e}{2mc}\,\mathbf{B}\cdot\mathbf{L}, \tag{2}$$

where the first term in H' is the 'optical potential' due to the electronic Coulomb interaction, which is periodic in the sense defined by Buxton *et al.* (1976), and the second term in H' is the interaction between electrons and the magnetic field contributed both from the pole piece and from the specimen. For convenience, the *z* axis of the magnetic domain is assumed to be along the optical axis of the microscope. Accordingly, the incident electron can be described as

$$|0\rangle=\exp(\mathrm{i}2\pi k_0 z). \tag{3}$$

Since the electron is accelerated to a very high speed, H' can be considered as a perturbation. From perturbation theory (Schiff 1968), the diffracted electrons, which can be viewed as a superposition of a set of plane waves

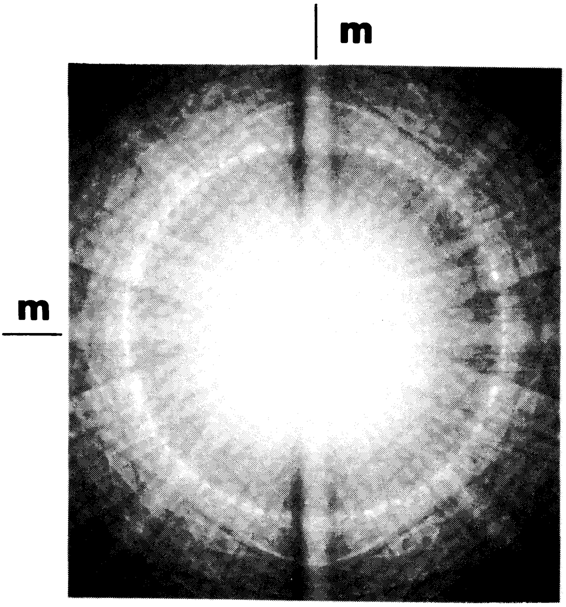
$$|\alpha\rangle=\exp(\mathrm{i}2\pi\mathbf{k}_\alpha\cdot\mathbf{r}),$$

are therefore given by

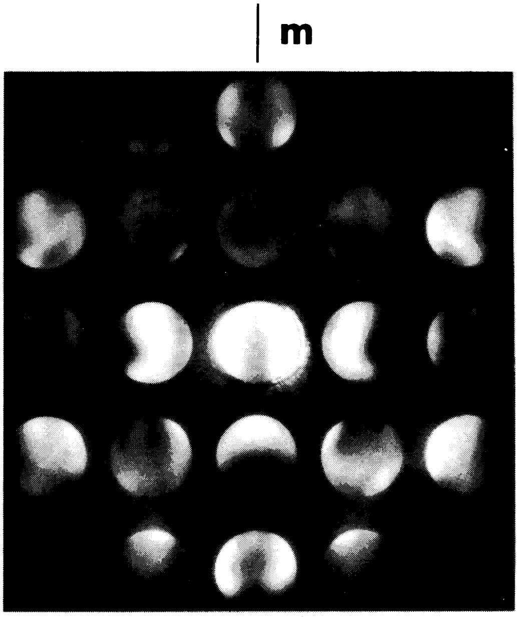
$$|\Psi\rangle=|0\rangle+\sum_\alpha f_{\alpha,0}|\alpha\rangle, \tag{4}$$

$$f_{\alpha,0}=-\frac{m}{2\pi h^2}\,\langle\alpha|H'|0\rangle. \tag{5}$$

Fig. 3



(*a*)



(*b*)

(*a*) Whole pattern of [11$\bar{2}$0] zone axes; and (*b*) the corresponding zero-layer disk.

When the magnetic field from both the pole piece and the magnetic specimen is in the z direction (the optical axis), we have

$$\mathbf{B}\cdot\mathbf{L}|0\rangle = BL_z|0\rangle = 0. \tag{6}$$

The physical meaning of ean. (6) is that the z component of the angular momentum is zero. This is expected, since the Lorentz force on the incident electron is zero in the described configuration. Combining eqns. (5) and (6), it is concluded that, under a first-order perturbation, the diffracted waves result only from the optical potential, which is invariant under the symmetry operation of the diffraction group 6mm. Thus the degeneracy from such invariance cannot be lifted by the magnetic field along the [0001] zone axis. In principle, this degeneracy can be lifted when higher-order perturbation terms are taken into account. The corresponding magnetic effect of the high-order perturbation term may possibly be observed in higher-order Laue zone (HOLZ) lines in the central disk of the [0001] zero-layer CBED pattern. Unfortunately, the HOLZ lines in our [0001] CBED pattern are not clear.

Nevertheless, this configuration, in which the zone axis under investigation is parallel to the magnetization of the specimen, is a special case. If the magnetic induction has a component perpendicular to the optical axis, eqn. (6) is not valid. That is, in general,

$$\langle\alpha|\mathbf{B}\cdot\mathbf{L}|0\rangle \neq 0.$$

This implies that the symmetry will break down due to the magnetic induction, and the observed diffraction group will correspond to $\frac{6}{\mathrm{m}}$ when the zone axes of the specimen are not parallel to the magnetic field of the specimen. This effect, originating from the perpendicular magnetic field, is maximized for zone axes which lie in the basal plane. In terms of the Lorentz force, it is evident because the velocity of incident electrons is perpendicular to the magnetic induction produced by the domain. This explains why the mirror symmetry from the mirror planes parallel to the c axis was lost in the zero-layer disks of the $[11\bar{2}0]$ CBED pattern.

In spite of the observed magnetic effect on the symmetry of zero-layer disks in CBED patterns, all whole patterns in our study appear to have the symmetry as if the $PrCo_5$ specimen were non-magnetic. This indicates that the diffraction is overwhelmed by the optical potential due to the Coulomb interaction in the specimen disregarding the large magnetic moment that the $PrCo_5$ compound has. It also implies that the zero-layer disks of CBED patterns are more sensitive to the diffracting potential than the corresponding whole patterns. Quantitatively, it is not fully understood how large the magnetic moment should be in order to see the magnetic effect in symmetry determination by CBED. In addition, it should be mentioned that the microscope alignment becomes more and more difficult as the specimen has a larger and larger magnetization component perpendicular to the optical axis. How the alignment could affect the symmetry determination in magnetic specimens needs further investigation.

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