Comment on 'Calculated chiral and magneto-electric dichroic signals for copper metaborate (CuB_2O_4) in an applied magnetic field'

2009 J. Phys.: Condens. Matter 21 498001

(http://iopscience.iop.org/0953-8984/21/49/498001)

J. Phys.: Condens. Matter **21** (2009) 498001 (3pp) doi:10.1088/0953-8984/21/49/498001

COMMENT

Comment on 'Calculated chiral and magneto-electric dichroic signals for copper metaborate (CuB_2O_4) in an applied magnetic field'

T Arima and M Saito

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

E-mail: arima@tagen.tohoku.ac.jp

Received 15 March 2009, in final form 7 September 2009
Published 19 November 2009
Online at stacks.iop.org/JPhysCM/21/498001

Abstract
Contrary to a claim by Lovesey and Staub (2009 *J. Phys.: Condens. Matter* **21** 142201), a careful treatment of symmetry shows that the application of a magnetic field along a twofold axis can induce the crystallographic chirality in a tetragonal system with the point group $\bar{4}2m$ like CuB_2O_4. The chirality is reversed by a 90° rotation of the magnetic field around the *c* axis.

In 2008 we reported a magnetic control of crystallographic chirality in copper metaborate (CuB_2O_4) [1]. A CuB_2O_4 crystal exhibits a circular dichroic signal for light propagating along the *c* axis in the presence of a magnetic field along the *a* axis in a canted antiferromagnetic phase between 10 and 21 K [2]. Because the reversal of the magnetic field does not affect the circular dichroic signal, it was assigned to time-reversal-even natural circular dichroism (NCD). Although the term 'natural' does not seem precise for the dichroic signal induced by the application of a magnetic field, we still refer to the signal as NCD to distinguish it from the conventional magnetic circular dichroism (MCD), which is a time-reversal-odd effect. For a magnetic field parallel to the *b* axis, the dichroic signal has the opposite sign, indicating the reversal of the crystallographic chirality. However, Lovesey and Staub claim in their recent fast track communication that the dichroic signals should not be attributed to NCD from the viewpoint of symmetry [3]. They also propose that the observed signal is likely caused by linear dichroism (LD). Here we point out a serious error in their treatment of crystallographic symmetry.

CuB_2O_4 is a tetragonal system with the non-enantiomorphic space group of $I\bar{4}2d$, belonging to the point group $\bar{4}2m$, in the paramagnetic phase without a magnetic field. In a tetragonal system with the point group $\bar{4}2m$, one twofold axis is interchanged with another twofold axis by fourfold rotoinversion (i.e., fourfold rotoreflection) or diagonal mirror reflection. Therefore, the two axes are equivalent. Yet, the two twofold axes must be distinguished from each other, because these symmetry operations flip the sense of a physical property related to chirality. For example, in an $AgGaS_2$ crystal with the $\bar{4}2m$ point group, the opposite sense of optical rotation was observed for the two twofold axes [4]. This behavior is common for all the $\bar{4}2m$ systems. Let us discuss not CuB_2O_4 with a very complicated structure but a simple molecule with the same point group, shown in figure 1. Figure 1(b) clearly indicates that the projections along the two twofold axes are distinct from each other, just like an enantiomorphic pair.

As discussed in the paper by Lovesey and Staub [3], CuB_2O_4 in a magnetic field along the *a* or *b* axis is described by the orthorhombic space (point) group of $I222$ (222)[1]. The point group 222 is known to allow enantiomorphism and NCD [5]. In other words, a crystal which belongs to this point group cannot be superimposed with its mirror image. Such an enantiomorphic pair of crystals exhibit an opposite sign of NCD.

Let us consider the (110) mirror image of a CuB_2O_4 crystal in the presence of a magnetic field along the *a* axis.

[1] Here, the time-reversal operation, often denoted by a prime, is not taken into account, because it is irrelevant to the crystallographic chirality and time-reversal-even NCD.

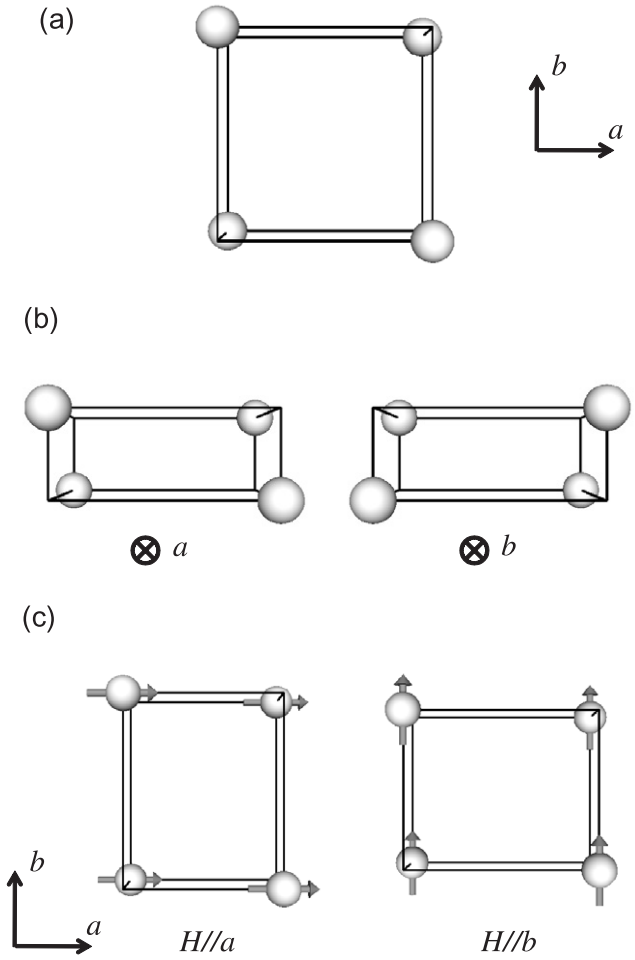

Figure 1. A compressed tetrahedron as one of the simplest molecules with the $\bar{4}2m$ (i.e., D_{2d}) point group. Boxes are guides to the eyes. (a) Perspective projection along the $\bar{4}$ axis. (b) Perspective projections along the two twofold axes. (c) Effect of the application of a magnetic field along (left) the *a* or (right) the *b* axis. Arrows indicate magnetic moments. Here we suppose that all the atoms are magnetic and that the molecule is compressed along the magnetic field direction because of the magnetic dipole–dipole interaction. The magnetic-field-induced distortion is exaggerated.

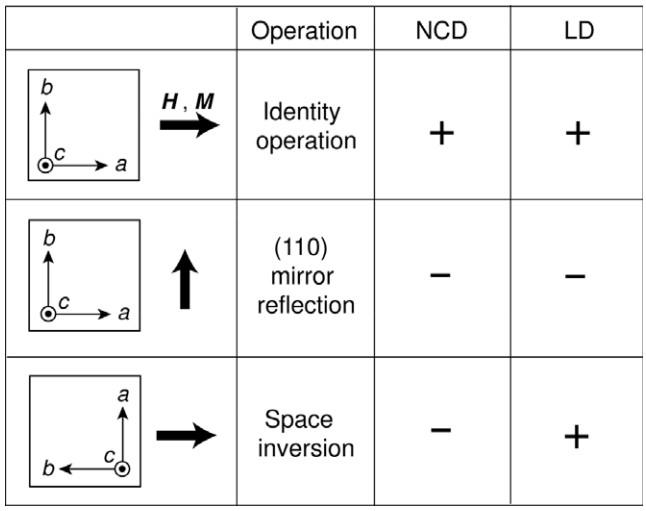

Figure 2. Effect of mirror reflection and space inversion on a copper metaborate crystal in the presence of a magnetic field along the *a* axis. The crystal in the field belongs to the point group 222, allowing both natural circular dichroism (NCD) and linear dichroism (LD), as shown in the first row. Its (110) mirror image and inversion image are shown in the second and third rows, respectively. Plus and minus in the columns for NCD and LD indicate that the sign of dichroic signal is unchanged and reversed, respectively.

The basic atomic arrangement of copper metaborate does not change with the mirror reflection, because the (110) diamond glide reflection is a symmetry operation for the paramagnetic phase. In other words, the mirror reflection does *not* switch the *a* and *b* axes, which was likely overlooked by Lovesey and Staub. In contrast, the reflection changes the magnetic field direction by 90°, as shown in the second row of figure 2. This clearly indicates that a CuB_2O_4 crystal in a magnetic field along the *b* axis is the mirror image of the crystal in a magnetic field along the *a* axis, although Lovesey and Staub mention that a magnetic field cannot execute a transition of an enantiomorphic form to its mirror image.

Another operation for producing an enantiomorphic pair is the space inversion. Let us first investigate the effect of the space inversion on the atomic arrangement. For the paramagnetic state, CuB_2O_4 has fourfold rotoinversion as a symmetry operation[2]. The space inversion after the fourfold rotoinversion is always identical to the fourfold rotation. Therefore, in a $\bar{4}2m$ system, where the fourfold rotoinversion is a symmetry operation, the space inversion is equivalent to the fourfold rotation about the *c* axis. On the other hand, the space inversion does not modify the magnetic field direction. As a result, the space inversion of a CuB_2O_4 crystal in a magnetic field corresponds to a 90° rotation of the crystal around the *c* axis retaining the magnetic field direction, as shown in the third row in figure 2. This also shows that CuB_2O_4 in the presence of a magnetic field along the *b* axis is the enantiomorphic pair of that in a magnetic field along the *a* axis.

The induction of chirality in a $\bar{4}2m$ system with the application of a magnetic field along a twofold rotation axis is also confirmed by considering the simple model in figure 1. Suppose that all the atoms have magnetic moments in the direction of a magnetic field. The dipole–dipole interaction can cause distortion of the molecule. Figure 1(c) exaggerates the distortion. One can see that the atomic arrangement becomes chiral with the point group 222. It can also be noted that the left and right panels in figure 1(c) cannot be superimposed by a 90° rotation around the *c* axis, indicating that they have the opposite sense of chirality to each other. Though the mechanism of the induction of the chirality in this case is different from our electronic model of canted antiferromagnetic CuB_2O_4 [1], this discussion is still useful in terms of symmetry.

Finally let us discuss LD of CuB_2O_4 in a magnetic field. As Lovesey and Staub point out, one should carefully examine whether the dichroic signal obtained contains an LD

[2] The conclusion does not change if one considers fourfold rotoreflection instead of fourfold rotoinversion.

component or not, because the application of a magnetic field lowers the crystal symmetry to orthorhombic.

A useful way to distinguish NCD from LD is to study the effect of space inversion. Since NCD is a parity-odd optical effect, the space inversion changes the sign of the NCD signal. On the other hand, the inversion does not affect parity-even LD. As discussed previously (see the third row of figure 2), the space inversion operation is equivalent to a rotation of the sample by 90° around the c axis without changing the magnetic field direction. Therefore, we measured NCD data by rotating a crystal in the presence of a horizontal magnetic field. A clear sign reversal of the dichroic signal for the $H \parallel a$ and $H \parallel b$ configurations evidently shows that the signal is attributable to NCD but not to LD. If one measures a change in dichroic signal with rotating a magnetic field by 90° around the beam (i.e. the c axis), as shown in the second row of figure 2, both NCD and LD change their sign. One cannot exclude a possible contamination of LD by this measurement. This behavior agrees with the well-known magnetic-field-induced optical anisotropy, often termed the Voigt effect or Cotton–Mouton effect. In a magnetic field perpendicular to the light propagation, generally, the optical constants can depend on whether the electric vector of light is parallel or perpendicular to the external magnetic field.

An estimation of the purity of circular polarization is also of importance. We performed a CD measurement for light propagation along the b axis by using the same system (see figure 3(e) in [1]). Copper metaborate, which is originally tetragonal, exhibits a large LD at around 1.4 eV in this configuration, because the corresponding excitation is only allowed for the c-polarized light [1, 6]. Nonetheless, no dichroic signal was discerned in the CD measurement, implying that the degree of linear polarization should be less than 0.1%. Such small linear polarization cannot produce a dichroic signal of the order of 1%, which is observed for light propagating along the c axis of a crystal subject to a magnetic field along the a or b axis.

In summary, a careful treatment of symmetry ascertains that a magnetic field can control the chirality of a $\bar{4}2m$ crystal. The circular dichroic signals that we previously reported cannot be ascribed to linear dichroism.

References

[1] Saito M, Ishikawa K, Taniguchi K and Arima T 2008 *Phys. Rev. Lett.* **101** 117402

[2] Petrakovskii G, Velikanov D, Vorotinov A, Balaev A, Sablina K, Amato A, Roessli B, Schefer J and Staub U 1999 *J. Magn. Magn. Mater.* **205** 105

[3] Lovesey S W and Staub U 2009 *J. Phys.: Condens. Matter* **21** 142201

[4] Hobden M V 1968 *Acta Crystallogr.* A **24** 676

[5] Klapper H and Hahn Th 2005 Space-group symmetry *Int. National Tables for Crystallography* 5th edn, vol A, ed Th Hahn (Dordrecht: Springer) pp 804–5

[6] Pisarev R V, Sänger I, Petrakovskii G A and Fiebig M 2004 *Phys. Rev. Lett.* **93** 037204