

Symmetry analysis of the structural and magnetic phase transitions in 122 iron arsenides

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Received 14 December 2011

Accepted 24 February 2012

It is evident from the literature that the 122 iron arsenides, $X\text{Fe}_2\text{As}_2$ with $X = \text{Ca}, \text{Sr}, \text{Ba}$ or Eu , undergo one or more phase transitions from a higher-temperature paramagnetic tetragonal structure in grey group $I4/mmm1'$ to an antiferromagnetic structure with magnetic space group $C_A mca$. Symmetry analysis is used to enumerate the possibilities for the transition (or transitions) between the higher- and lower-symmetry structures, and the results are used as a basis for comment on published experimental results.

The 122 iron arsenides, $X\text{Fe}_2\text{As}_2$ with $X = \text{Ca}, \text{Sr}, \text{Ba}$ and Eu , are attracting intense interest consequent upon the observation of superconductivity in these materials. They represent a subclass of iron-based superconductors, the first of which, $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ with critical temperature T_c at 26 K, was discovered just 3 years ago (Kamihara *et al.*, 2008). This discovery motivated a great deal of further research, in part in an effort to obtain higher critical temperatures, but also in the belief that studies of this new class of (copper-free) superconductors would lead to greater insights into the mechanisms of high-temperature superconductivity. It was soon discovered that the 122 iron arsenides also could be superconducting: the hole-doped iron arsenide $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with $x \simeq 0.4$ was found to be superconducting with T_c at 38 K (Rotter *et al.*, 2008), and superconductivity was reported in the electron-doped iron arsenides $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ (Sefat *et al.*, 2008) and $\text{SrFe}_{2-x}\text{Co}_x\text{As}_2$ (Leithe-Jasper *et al.*, 2008) with T_c of 22 and 19 K at $x \simeq 0.2$. It was also found that the undoped iron arsenides CaFe_2As_2 (Park *et al.*, 2008; Torikachvili *et al.*, 2008), SrFe_2As_2 , BaFe_2As_2 (Alireza *et al.*, 2009) and EuFe_2As_2 (Miclea *et al.*, 2009; Terashima *et al.*, 2009) become superconducting under pressure, for example a T_c of 29 K was recorded in a sample of BaFe_2As_2 under a pressure of ~ 4 GPa (Alireza *et al.*, 2009).

These observations of superconductivity have generated renewed interest in the structural and magnetic phase transitions in the 122 iron arsenides, even though it is generally agreed (Pickett, 2009) that to achieve superconductivity these transitions need to be suppressed. The room-temperature structures of SrFe_2As_2 , BaFe_2As_2 and EuFe_2As_2 have long been known to be tetragonal in the space group $I4/mmm$ (Pfisterer & Nagorsen, 1980; Marchand & Jeitschko, 1978). That CaFe_2As_2 adopts the same structure seems to have been established only very recently, following the interest in its superconductivity (Ni *et al.*, 2008; Kreyssig *et al.*, 2008). Certainly the connection with superconductivity has motivated studies of the low-temperature crystal and magnetic structures, which previously had been largely unexplored. It has been found that all the $X\text{Fe}_2\text{As}_2$ structures, with $X = \text{Ca}, \text{Sr}, \text{Ba}$ and Eu at ambient pressure, undergo a distortion below room temperature to an orthorhombic structure that is described in the space group $Fmmm$. The orthorhombic lattice vectors $\mathbf{a}_o, \mathbf{b}_o, \mathbf{c}_o$ are related to those of the tetragonal structure $\mathbf{a}_t, \mathbf{b}_t, \mathbf{c}_t$ by $\mathbf{a}_o = \mathbf{a}_t + \mathbf{b}_t, \mathbf{b}_o = -\mathbf{a}_t + \mathbf{b}_t, \mathbf{c}_o = \mathbf{c}_t$. The reported transition temperatures are 170 K for CaFe_2As_2 (Ni *et al.*, 2008), 202 K for SrFe_2As_2 (Li *et al.*, 2009; Tegel *et al.*, 2008), 136 K in BaFe_2As_2 (Wilson *et al.*, 2009) and 190 K in EuFe_2As_2 (Tegel *et al.*, 2008; Raffius *et al.*, 1993). These compounds have also been found to be anti-

ferromagnetic at low temperatures, the moments being parallel and antiparallel to \mathbf{a}_o , coupled ferromagnetically along the orthorhombic b axis, and coupled antiferromagnetically along the orthorhombic a and c axes (see Fig. 1). With the aid of the visualization features of the program *ISODISTORT* (Campbell *et al.*, 2006) we have recognized the magnetic space-group symmetry as B_Abcm (in a standard setting this would be C_{Amca}). The reader is invited to check our identification of the magnetic symmetry by comparing the structure shown in our Fig. 1, drawn in B_Abcm using *ATOMS* (Dowty, 1999), with that shown in Fig. 2 of Goldman *et al.* (2008).

Two questions arise about the transition(s) between the room-temperature paramagnetic tetragonal structure and the low-temperature antiferromagnetic one. Is this a single transition, or are there two transitions – one structural and one magnetic? Also, is the transition [are the transition(s)] continuous in nature or first order? The structural and magnetic transition(s) in CaFe_2As_2 are said to be coincident (or essentially so) and first order (Ni *et al.*, 2008; Goldman *et al.*, 2008; Baek *et al.*, 2009) and the behaviour in SrFe_2As_2 appears to be similar (Li *et al.*, 2009; Tegel *et al.*, 2008; Zhao *et al.*, 2008; Yan *et al.*, 2008; Jesche *et al.*, 2008). There has been more debate on the situation in BaFe_2As_2 . The earliest reports (Huang *et al.*, 2008) were of simultaneous first-order structural and magnetic transitions as in the compounds mentioned just above. It was claimed in subsequent work (Wilson *et al.*, 2009) that the structural and magnetic transitions are simultaneous but second order. This claim was retracted (Rotundu *et al.*, 2010) for well annealed samples, while very recently (Kim *et al.*, 2011) there is a claim of two separate transitions, a second-order structural transition at 134.5 K and a first-order magnetic transition at 133.75 K. The magnetic structures of the compound EuFe_2As_2 had been studied earlier, the original interest being derived from the presence of two magnetic species, Fe and Eu. It shows two magnetic ordering transitions, a higher one associated with the magnetic ordering of the Fe atoms and a lower associated with the ordering of the Eu (Raffius *et al.*, 1993). Recent studies of the higher transition suggest that the structural transition and the

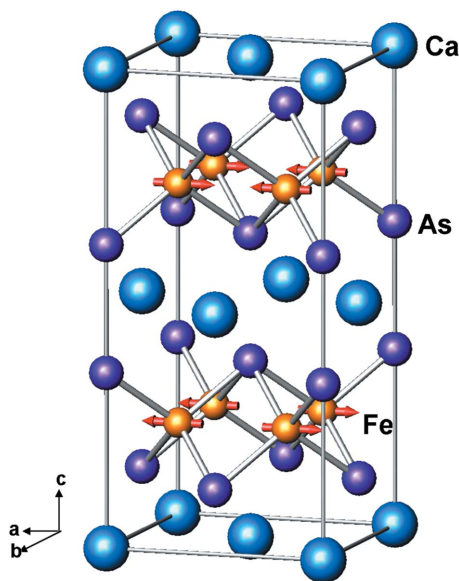


Figure 1
The structure of CaFe_2As_2 drawn using the computer program *ATOMS* (Dowty, 1999), assuming magnetic space-group symmetry B_Abcm . The lattice parameters and atomic coordinates are taken from Goldman *et al.* (2008).

magnetic ordering of the Fe coincide, and the transition(s) is (are) probably first order (Jeevan *et al.*, 2008; Xiao *et al.*, 2009; Koo *et al.*, 2010).

In this communication the purpose is to use group theory, as implemented in computer programs *ISOTROPY* (Stokes *et al.*, 2007) and *ISODISTORT* (Campbell *et al.*, 2006), to examine the various possibilities for transition(s) between the paramagnetic tetragonal structure in $I4/mmm$ (grey group $I4/mmm1'$) and the antiferromagnetic structure in B_Abcm . Similar approaches have proved profitable in other applications, such as in the study of structures and phase transitions in perovskites (Howard & Stokes, 2005). The mechanics of using these programs is explained in detail in Stokes *et al.* (2007), Campbell *et al.* (2006) and Howard & Stokes (2005), and will not be shown here. The pertinent results can be summarized as follows:

(i) The antiferromagnetic structure in B_Abcm can arise directly from the magnetic distortion associated with the two-dimensional irreducible representation (irrep¹) mX_2^+ at the X -point ($\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$) of the Brillouin zone. The required structure is obtained for the order-parameter direction (a, a) .² As expected, the lattice vectors of the orthorhombic antiferromagnetic structure are related to those of the starting tetragonal structure by $\mathbf{a}_o = \mathbf{a}_t + \mathbf{b}_t$, $\mathbf{b}_o = -\mathbf{a}_t + \mathbf{b}_t$, $\mathbf{c}_o = \mathbf{c}_t$. The transition is allowed to be continuous in Landau theory, but is not required to be so. There is a linear-quadratic coupling of the strains $e_{11} + e_{22}$, e_{33} and e_{12} (strains defined with respect to the tetragonal parent) with M^2 , M being the magnetic order parameter that we presume can be identified with the magnetic moment carried by the Fe atom. Strain e_{12} in its turn breaks the tetragonal symmetry (meaning \mathbf{a}_t is no longer perpendicular to \mathbf{b}_t) and so drives the distortion to the metrically orthorhombic cell. A linear-quadratic coupling of the shear strain with the magnetic order parameter has been suggested elsewhere (Barzykin & Gor'kov, 2009; Cano *et al.*, 2010).

(ii) A structural transition might precede the magnetic transition (on lowering the temperature). The structural transition would be from tetragonal $I4/mmm$ to the orthorhombic structure in $Fmmm$ (with the usual relationships between lattice vectors), and would be a proper or pseudo-proper ferroelastic transition associated with the irrep Γ_4^+ at the Brillouin zone centre. The transition would in effect be driven by a spontaneous strain (defined with respect to the tetragonal parent) e_{12} . The transition is allowed to be continuous in Landau theory, but is not required to be so. There would follow a magnetic transition from grey group $Fmmm1'$ to B_Abcm , the magnetic distortion being associated with irrep mY_2^+ at the Y -point ($\mathbf{k} = 0, 1, 0$) of the Brillouin zone for the $Fmmm$ structure. This transition is also allowed to be continuous, but is not required to be so. There is linear-quadratic coupling of the strains e_{11} , e_{22} , e_{33} (now defined with respect to the orthorhombic cell) with M^2 , but none of these strains break the orthorhombic symmetry established at the prior structural transition.

(iii) The magnetic transition might precede the structural transition. The magnetic transition would have all the characteristics described under scenario (i), and would by itself lower the symmetry to orthorhombic. Accordingly, a subsequent structural transition to the final orthorhombic structure would be an isosymmetric transition and would be expected to be first order (Stokes *et al.*, 2007; Christy, 1995).

¹ We will use the notation of Miller & Love (1967).

² Order-parameter direction (a,b) , $a \neq b$, gives a lower symmetry antiferromagnetic structure, magnetic space-group symmetry P_Cbam , in which moments remain in the orthorhombic ab plane, but are no longer collinear.

It is of interest to examine a selection of published experimental data in the light of these results.

Consistent with scenario #1, some authors (Huang *et al.*, 2008; Kim *et al.*, 2011) have directly implicated a spin density wave at $\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$ (tetragonal) in the transitions occurring. As mentioned above, there are many reports that the structural and magnetic transitions coincide, but fewer authors suggest that the orthorhombic distortion is due to linear-quadratic coupling of the strain with the magnetic order parameter. Koo *et al.* (2010), in a study of EuFe_2As_2 , suggest that Fe magnetic order drives the structural phase transition *via* linear-quadratic coupling (Barzykin & Gor'kov, 2009; Cano *et al.*, 2010) and have shown from their measurements that the strain³ varies with the square of the magnetic order parameter, as would be expected. In another study on EuFe_2As_2 (Xiao *et al.*, 2009), the width of the orthorhombic (040) reflection, taken to represent the strain, seems to have temperature dependence similar to that of the intensities of magnetic reflections, taken to represent the square of the magnetic order parameter. Although the data have not been analysed in this way, they would seem to be consistent with linear-quadratic coupling of the strain to the magnetic moment. Jesche *et al.* (2008) studied the coupling in SrFe_2As_2 using X-rays to examine the strain and muon spin-relaxation spectroscopy to determine magnetic moments, and claimed the strain was directly proportional to the magnetic moment; bilinear coupling to a magnetic order parameter is not allowed so the result is simply not credible. It may be that the muon precession frequency is proportional not to the magnetic moment as claimed, but to the square of that moment. Wilson *et al.* (2009), however, found a similar result in BaFe_2As_2 . They found something akin to bilinear coupling but, being aware that this is symmetry forbidden, they ascribed it to biquadratic coupling instead. They were led to conclude that the structural distortion was not driven by the magnetic ordering but was an independent ferroelastic instability – even if this were the case it is difficult to imagine that there would not be a significant linear-quadratic coupling of the strain to the magnetic order parameter. It may be significant in this context that the results for strain reported by Wilson *et al.* (2009) were obtained from neutron single-crystal studies of modest resolution, and they have since been superseded by results from high-resolution X-ray diffraction at a synchrotron facility (Rotundu *et al.*, 2010). The group theory indicates that a single transition as described in scenario #1 can be continuous, but is not required to be so. The experimental data on this point are so far ambiguous.

There seem to be just a few reports in the 122 iron arsenides of a structural transition preceding a magnetic transition, as described in scenario #2. Results for SrFe_2As_2 presented by Zhao *et al.* (2008) in their Fig. 2 can be taken to suggest a discontinuous structural transition followed immediately by a continuous magnetic one. Such a result is certainly allowed under scenario #2. By contrast, for BaFe_2As_2 , Kim *et al.* (2011) have attempted determination of structural and magnetic order parameters using combined simultaneous high-resolution X-ray diffraction and X-ray resonant magnetic scattering, and have drawn different conclusions. They find a second-order structural transition at 134.5 K, followed by a discontinuous magnetic transition at 133.75 K. The first-order magnetic transition is taken to drive a discontinuity in the orthorhombic distortion.

The authors are not aware of any reports that put the magnetic transition higher than the structural transition, as proposed here in scenario #3.

In this communication we have given, we believe for the first time, the magnetic space-group symmetry for the low-temperature magnetic structure of the 122 iron arsenides. Although a simple symmetry analysis does not address open questions on the microscopic mechanisms, it can provide a basis for assessing the published experimental results. Questions on the coupling of orthorhombic strain with magnetic moment [and by implication on the nature of the transition(s)] are not fully resolved by the existing experimental data; in this respect the authors believe further studies yielding simultaneous high-quality data on both strain and magnetic moment would be well worth while. A complete analysis of coupling between order parameters related to irreps Γ_4^+ and mX_2^+ , with direct mechanisms and indirect mechanisms through the common strain, will provide a model for testing whether the structural component can indeed drive a separate phase transition or whether it merely follows the magnetic ordering as a secondary order parameter. In particular, linear-quadratic coupling between the two order parameters leads to quite different patterns of evolution depending on the strength of coupling and on whether the two possible instabilities have similar or widely separated critical temperatures (Salje & Carpenter, 2011).

One of us (CJH) thanks Professor Erich Kisi for useful discussions during the preparation of this manuscript.

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³ These and other authors define strain as $(a - b)/(a + b)$, where a and b are cell dimensions in orthorhombic structure. It can be shown that ϵ_{12} is proportional to this quantity.

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