The EFG Tensor at High Symmetry Sites in Crystals

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May 22, 2007

The electric field gradient or EFG is the tensor of mixed second partial derivatives of the electrostatic potential[1],

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}.$$

It is thus a symmetric second rank tensor. Furthermore it has zero trace, since V satisfies the Laplace equation. Conventionally, the principle axes (x, y, z) are defined so that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|.$$

And *axial symmetry* is defined by nonzero η where

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

Here, I am interested in how to tell, by crystal symmetry, whether V_{ij} is axial or not. When the site in question has a 3-fold or 4-fold axis of symmetry, then the EFG is axial, but it seems that the quasitetrahedral site in the BCC lattice (e.g. at $Q = (0.5, 0.25, 0)$) is also axial with the principle axis z along $\langle 010 \rangle$[2], so while the former criterion is sufficient it is not necessary. The Q site mentioned above is along the intersection line of 2 orthogonal mirror planes: the basal plane parallel to $\langle 001 \rangle$ and the plane parallel to $\langle 100 \rangle$ that runs through the centre of the conventional cubic unit cell. The intersection of these mirror planes is a line parallel to $\langle 010 \rangle$ running through the middle of the face and is apparently the principle axis of the EFG. It is a 2-fold axis, but it also has another symmetry: rotate by $\pi/2$ and then reflect through a plane parallel to $\langle 010 \rangle$ that runs through the point Q, i.e. a fourfold rotation-reflection axis (an improper point symmetry also called an improper rotation).

While V_{ij} appears superficially to have 9 independent components, because it is symmetric and traceless there must only be 5. In fact it is even simpler, since V_{ij} can always be diagonalized by appropriate choice of coordinate system. Thus there are really only two degrees of freedom, i.e. V_{zz} and η.

While the analysis of tensors can be quite involved[3], here I will summarize how to sort out the symmetry of the EFG in a simple straightforward way for this example of the Q site, following the discussion of Bhatia and Singh[4]. First we express V_{ij} in the conventional cubic

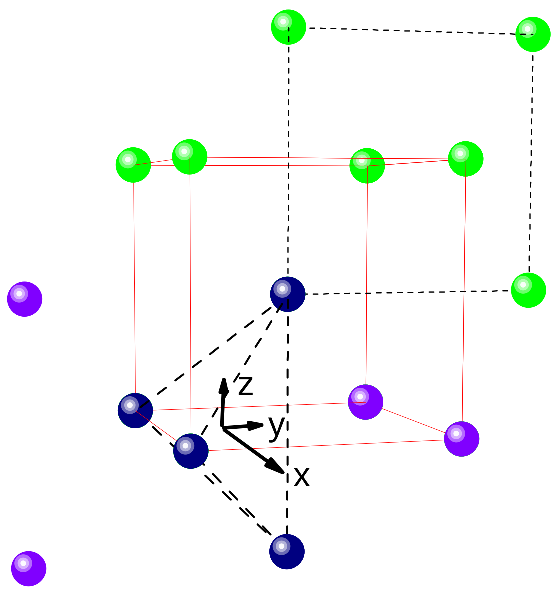

Figure 1: The coordinate system for the Q at $(0.5, 0.25, 0)$ relative to the corner of the conventional cubic unit cell. We define the coordinate system with the origin at this site as shown.

coordinate system (see Fig.1) of the BCC lattice noting that this may not be the principle axis system. Thus

$$V_{ij} = \begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix},$$

where symmetry is explicit, and we recognize that $a + b + c = 0$.

Before the improper rotation, let's consider the simplifications coming from other symmetries of the Q-site. First note that the xy plane is a mirror plane of the crystal. Thus reflecting through xy we end up in an equivalent situation, i.e. in the mirrored coordinate system, the tensor $V'_{ij} = V_{ij}$. The mirrored coordinate system can be obtained via

$$\mathbf{x}' = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \mathbf{A}\mathbf{x}.$$

The coordinate transformation matrix for the reflection is its own inverse, i.e. $\mathbf{A}^{-1} = \mathbf{A}$. Using the rules of the transformation of a second rank tensor,

$$\begin{aligned} V'_{ij} &= \mathbf{A}^{-1} V_{ij} \mathbf{A} \\ &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{aligned}$$

$$
\begin{aligned}
&= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a & d & -e \\ d & b & -f \\ e & f & -c \end{bmatrix} \\
&= \begin{bmatrix} a & d & -e \\ d & b & -f \\ -e & -f & c \end{bmatrix}.
\end{aligned}
$$

Now we use $V'_{ij} = V_{ij}$ to easily obtain $e = -e$ and $f = -f$, i.e. $e = f = 0$ which simplifies V_{ij} to

$$
V_{ij} = \begin{bmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{bmatrix}.
$$

Next we note that the yz plane is also a mirror plane. A similar argument to the above yields $d = 0$ and

$$
V_{ij} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix}.
$$

Thus in the conventional coordinate system, V_{ij} is diagonal, i.e. xyz **is the principle axis system**. It is worth noting that the occurrence of two orthogonal mirror planes will always yield such a conclusion.

Now let's consider the 4-fold roto-reflection axis which for this site is the y axis (see Fig.1). The (right-handed) symmetry operation brings x to $x' = z$, y to $y' = -y$ and z to $z' = -x$, so the coordinate transform matrix is

$$
\mathbf{A} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix}.
$$

In this case the inverse $\mathbf{A}^{-1}$ is the transpose $\mathbf{A}^T$, which is easily demonstrated:

$$
\mathbf{A}\mathbf{A}^T = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{I}.
$$

Thus

$$
\begin{aligned}
V'_{ij} &= \mathbf{A}^{-1} V_{ij} \mathbf{A} \\
&= \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \\
&= \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & a \\ 0 & b & 0 \\ -c & 0 & 0 \end{bmatrix}
\end{aligned}
$$

$$= \begin{bmatrix} c & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & a \end{bmatrix}.$$

Again we use $V'_{ij} = V_{ij}$ to obtain $c = a$, i.e.

$$V_{ij} = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & a \end{bmatrix},$$

that is, the EFG principle axis is y and the EFG is cylindrically symmetric about this axis ($\eta = 0$). This example shows how to easily constrain the EFG by site symmetry.

References

[1] M.H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 321.

[2] B. Ittermann *et al.*, Z. Phys. B **91**, 7 (1993).

[3] "Tensor Properties of Crystals" by D.R. Lovett (IOP, London, 1989).

[4] A.B. Bhatia and R.N. Singh, "Mechanics of Deformable Media" (Hilger, Bristol, 1986), §3.7, p. 40