Co and Pr atoms are magnetically ordered. Therefore the conclusion that it is the Pr atoms which give rise to the magnetic scattering, in spite of their apparently high moment, rests rather heavily on what has been found in structurally related materials. Neutron diffraction patterns of YCo_2Ge_2 at RT and LT measured in the course of this work are essentially the same. We also studied the compound $NdCo_2Ge_2$ that belongs to the same series. The neutron diffraction patterns indicate the existence of magnetic ordering at 28 ± 1 K, but the magnetic structure seems different and much more complicated; in view of the poorness of the data, we are not able, for the moment, to solve it.

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Refinement of Metal *d*-Orbital Occupancies from X-ray Diffraction Data*

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Abstract

Expressions are derived relating the occupancies of transition-metal *d* orbitals in a trigonal distortion of an octahedral field to the populations of multipole density functions refined from X-ray diffraction data. The expressions are used to obtain the iron *d*-orbital configuration in cubic FeS_2 by least-squares refinement of very high resolution single-crystal X-ray intensity measurements. The refined populations correspond to a large distortion of the iron electron density from spherical symmetry towards a low-spin configuration.

Introduction

Compounds containing transition-metal atoms have been the subject of a number of recent experimental electron-density determinations using accurate X-ray (and neutron) diffraction measurements (for example Iwata, 1977; Iwata & Saito, 1973; Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Rees & Mitschler, 1976; Vicat, Tranqui & Aleonard, 1977; Wang & Coppens, 1976). Deviations from a spherical density distribution are generally found about the metal atom which can often be interpreted qualitatively in terms of partial occupancy of the *d* orbitals.

A more quantitative description of the electronic structure of the metal atom may be obtained by fitting the charge distribution with a small number of analytical density functions. Several models are currently in use for describing the electron density distribution in crystals with a series of atom-centered multipole functions (Hansen & Coppens, 1978; Harel & Hirshfeld, 1975; Stewart, 1976). Within the limits of the crystal field theory which neglects covalent interactions between the metal atom and ligands, simple relationships between populations of spherical harmonic functions on metal atoms and *d*-orbital occupancies can be derived. As an example, the relationships for a metal atom on a $\bar{3}m$ site are derived here and applied to the analysis of single-crystal diffraction data from iron pyrite (Stevens, DeLucia & Coppens, 1979).

Orbital products

For a trigonal distortion from octahedral symmetry (Ballhausen, 1962), it is convenient to express the

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* Electron Population Analysis of Accurate Diffraction Data. VIII. Part VII: Coppens, Guru Row, Leung, Stevens, Becker & Yang (1979).

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angular component of the d orbitals in terms of spherical harmonic functions in real form, $y_{lm\pm}$, as follows:

$$\begin{aligned}
&(a_g) && y_{20},\\
&(e_{g+}) && (\tfrac{2}{3})^{1/2}y_{22+} - (\tfrac{1}{3})^{1/2}y_{21+},\\
&(e_{g-}) && (\tfrac{2}{3})^{1/2}y_{22-} + (\tfrac{1}{3})^{1/2}y_{21-},\\
&(e_{g+})' && (\tfrac{1}{3})^{1/2}y_{22+} + (\tfrac{2}{3})^{1/2}y_{21+},\\
&(e_{g-})' && (\tfrac{1}{3})^{1/2}y_{22-} - (\tfrac{2}{3})^{1/2}y_{21-}.
\end{aligned} \tag{1}$$

Here the threefold axis is taken as the axis of quantization (z axis) and the x axis is chosen so that one of the ligands lies in the xz plane. The (e_{g-}), (a_g), and (e_{g+}) orbitals correspond to the three t_{2g} orbitals, and the $(e_{g-})'$ and $(e_{g+})'$ orbitals to the two e_g orbitals of the octahedral point group.

If the atomic wavefunction is expressed in the form of a linear combination of Slater determinants, integration over all spin coordinates and the space coordinates of all electrons but one gives the one-electron density distribution, $\rho(r) = \sum_\mu \sum_\nu P_{\mu\nu}\varphi_\mu\varphi_\nu$ where the $P_{\mu\nu}$ are non-integer population coefficients and the φ_μ are atomic orbitals or linear combinations of atomic orbitals.

Let us assume that the density near the transition-metal atom may be approximated by the sum of the densities of the unperturbed core, the 3d shell, and the 4s shell, $\rho(r) = \rho_{\rm core} + \rho_{3d} + \rho_{4s}$. If P_1, P_2 and P_3 are taken as the occupancies of the a_g, e_g, and e_g' orbitals respectively, then the d-shell density will be given by

$$\begin{aligned}
\rho_{3d}(\mathbf{r}) = [R(r)]^2\{&P_1(a_g)^2 + \tfrac{1}{2}P_2[(e_{g-})^2 + (e_{g+})^2]\\
&+ \tfrac{1}{2}P_3[(e_{g-}')^2 + (e_{g+}')^2]\},
\end{aligned} \tag{2}$$

where $R(r) = Nr^2\exp(-\zeta r)$ is the radial function of the d orbitals and averaging over the degenerate orbitals is assumed. Additional terms for which $\mu \neq \nu$ only occur in this expression as far as allowed by the point group symmetry (see below).

The products of the spherical harmonic functions in (2) are again spherical harmonics. When the appropriate expressions (Rose, 1957; Rae, 1978) are substituted we obtain:

$$\begin{aligned}
\rho_d(\mathbf{r}) = [R(r)]^2[&(P_1 + P_2 + P_3)(1/4\pi)^{1/2}M_{00}y_{00}\\
&+ (2P_1 - P_2)(5/196\pi)^{1/2}M_{20}y_{20}\\
&+ (6P_1 - \tfrac{2}{3}P_2 - \tfrac{7}{3}P_3)(1/196\pi)^{1/2}M_{40}y_{40}\\
&+ (P_3 - P_2)(5/63\pi)^{1/2}M_{43}y_{43+}],
\end{aligned} \tag{3}$$

where M_{lm}, the ratio of normalization factors for wavefunctions and density functions defined by $M_{lm} = N_{lm}(\text{wavefunction})/N_{lm}(\text{density function})$, occurs because the density functions in (3) are normalized differently than the orbital functions in (2) (Hansen & Coppens, 1978). The four terms in (3) correspond to the four allowed multipole functions at the distorted octahedral ($\bar{3}m$) site. Each term will be determined by refinement of the density function population parameters, P_{lm}, which are related to the orbital occupancies P_1, P_2, and P_3 by the expressions:

$$\begin{aligned}
P_{00} &= (P_1 + P_2 + P_3)(1/4\pi)^{1/2}M_{00},\\
P_{20} &= (2P_1 - P_2)(5/196\pi)^{1/2}M_{20},\\
P_{40} &= (6P_1 - \tfrac{2}{3}P_2 - \tfrac{7}{3}P_3)(1/196\pi)^{1/2}M_{40},\\
P_{43+} &= (P_3 - P_2)(5/63\pi)^{1/2}M_{43}.
\end{aligned} \tag{4}$$

Equations (4) may be solved in terms of the orbital population to give

$$\begin{aligned}
P_1 &= \tfrac{1}{5}P_{00} + \tfrac{2}{5}A_{20}P_{20} - \tfrac{1}{5}A_{43}P_{43+},\\
P_2 &= \tfrac{2}{5}P_{00} - \tfrac{1}{5}A_{20}P_{20} - \tfrac{2}{5}A_{43}P_{43+},\\
P_3 &= \tfrac{2}{5}P_{00} - \tfrac{1}{5}A_{20}P_{20} + \tfrac{3}{5}A_{43}\mathrm{P}_{43+},
\end{aligned} \tag{5}$$

where

$$A_{20} = (196\pi/5)^{1/2}/M_{20}$$

and

$$A_{43} = (63\pi/5)^{1/2}/M_{43}.$$

Since there are four multipole functions but only three unknowns (P_1, P_2 and P_3), a constraint may be imposed on the multipole populations, which was chosen as

$$P_{40} = (\tfrac{7}{3}A_{43}P_{43+} + 3A_{20}P_{20})/A_{40}, \tag{6}$$

where

$$A_{40} = (196\pi)^{1/2}/M_{40}.$$

If the atomic wavefunction would be a single Slater determinant, the occupation parameters should be integers since each orbital would be occupied by only 0, 1, or 2 electrons. However, for any significant distortion from octahedral symmetry, the e_g and e_g' orbitals belong to the same symmetry representation and may mix given new orbitals, $\varphi_1 = C_1(e_{g+}) + C_2(e_{g+})'$ and $\varphi_2 = C_1(e_{g-}) + C_2(e_{g-})'$, which are linear combinations of the original basis set. Thus, the products $(e_{g+})(e_{g+})'$ and $(e_{g-})(e_{g-})'$ are introduced into the expression for the one-electron density.

If we include a new parameter, P_4 for the cross product of e_g and e_g', and substitute the appropriate expression for products of spherical harmonic functions, (4) becomes

$$\begin{aligned}
P_{00} &= (P_1 + P_2 + P_3)(1/4\pi)^{1/2}M_{00},\\
P_{20} &= (2P_1 - P_2 - \sqrt{2}P_4)(5/196\pi)^{1/2}M_{20},\\
P_{40} &= (6P_1 - \tfrac{2}{3}P_2 - \tfrac{7}{3}P_3 + 5\sqrt{2}/3P_4)(1/196\pi)^{1/2}M_{40},\\
P_{43+} &= (P_3 - P_2 + \tfrac{1}{3}P_4)(5/63\pi)^{1/2}M_{43},
\end{aligned} \tag{7}$$

and the constraint in (6) is not imposed.

Solving these equations gives

$$
\begin{aligned}
P_1 &= \tfrac{1}{5}P_{00} + \tfrac{1}{7}A_{20}P_{20} + \tfrac{3}{35}A_{40}P_{40},\\
P_2 &= \tfrac{2}{5}P_{00} - \tfrac{5}{7}A_{20}P_{20} + \tfrac{6}{35}A_{40}P_{40} - \sqrt{2}P_4,\\
P_3 &= \tfrac{2}{5}P_{00} + \tfrac{4}{7}A_{20}P_{20} - \tfrac{9}{35}A_{40}P_{40} + \sqrt{2}P_4,\\
P_4 &= \frac{3}{6\sqrt{2}+1}\left(-\tfrac{9}{7}A_{20}P_{20} + \tfrac{3}{7}A_{40}P_{40} + A_{43}P_{43+}\right).
\end{aligned}
\tag{8}
$$

Results

High-resolution ($\sin\theta_{\max}/\lambda = 1{\cdot}45$ Å^{-1}) single-crystal X-ray intensity measurements were collected at room temperature from a 0·09 mm sphere of natural pyrite using Pd-filtered Ag $K\alpha$ radiation. A detailed analysis of the electron-density distribution in pyrite is given by Stevens, DeLucia & Coppens (1979). The iron atom in cubic FeS_2 (space group $Pa3$) is at a $\bar{3}$ site, with the six near-neighbor sulfur atoms forming a trigonally distorted octahedron about the iron. The local symmetry is therefore $\bar{3}m$. As the population of the additional multipole function, y_{43-}, allowed for a $\bar{3}$ site refined to within one standard deviation of zero in all early refinements, $\bar{3}m$ symmetry was adopted in subsequent runs. The refinements also include (as allowed by symmetry) multipole parameters on sulfur, positional parameters, anisotropic and anharmonic [third and fourth cumulants (Johnson, 1969)] thermal parameters for both atoms, an isotropic secondary extinction parameter, and the radial dependence ζ of the multipole parameters.

Since the iron 4*s* orbital contributes very little to the X-ray scattering, its population cannot be reliably determined, and has been assumed to be zero in these refinements. The results of several refinements are listed in Table 1. In refinement (I), the multipoles have been fixed corresponding to a spherical atom model for comparison. In (II), the total population of the iron 3*d* shell has been fixed at 6·0 e. In all cases, the populations are constrained to maintain electroneutrality in the crystal. Estimated standard deviation in the orbital occupancies have been calculated from the least-squares variance–covariance matrix and include the correlations between the refined multipole parameters.

Table 1. *Orbital occupancies of* Fe *in pyrite from refinement of X-ray data*

	Refinement		
	(I)	(II)	(II)
ζ(a.u.$^{-1}$)	3·73 (3)	3·79 (3)	3·93 (4)
$P_{3d}(=P_1+P_2+P_3)$	6·00	6·0	5·22 (13)
$P(S_2)$	2·00	2·0	2·77 (13)
P_1	1·2	1·98 (12)	1·82 (13)
P_2	2·4	3·36 (15)	3·06 (17)
P_3	2·4	0·66 (15)	0·34 (17)
P_4	0·0	−0·04 (16)	0·02 (16)
$R(F)$ (%)	2·35	1·81	1·79
$R_w(F)$ (%)	1·92	1·31	1·29

For a low-spin configuration of iron with pure octahedral coordination, the expected values of P_1, P_2, and

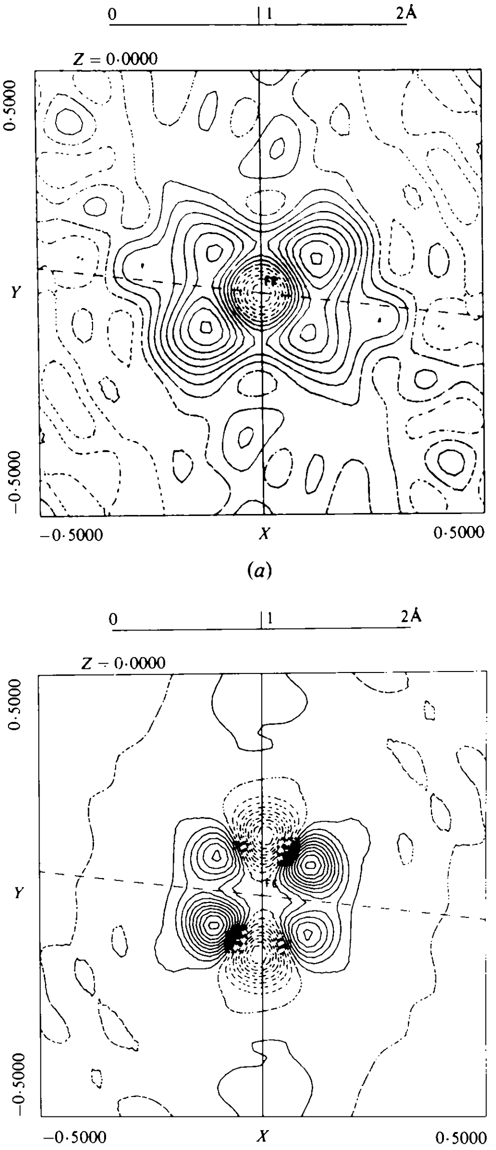

Fig. 1. Deformation density about the iron atom in FeS_2. (*a*) Experimental density minus isolated, spherical atom densities calculated with parameters from a high-order refinement and including structure factors with $F > 3\sigma(F)$ to a $\sin\theta/\lambda$ resolution of 1·20 Å^{-1}. (*b*) Model density given by the refined multipole populations including thermal smearing. The plane is defined by three points; the iron position, the position of one of the sulfur atoms, and the midpoint of the line joining the other two sulfur atoms related to the first by the threefold axis. Two of the six sulfur atoms lie in the plane in the directions defined by the solid line and the other four lie above and below the broken line. The plane contains four of the eight maxima in the $(a_g)^2 + (e_g)^2$ density and the threefold axis passing diagonally through the iron atom and the two higher peaks. Contours are plotted at 0·20 e Å^{-3} with negative contours dashed.

P_3 are 2·0, 4·0, and 0·0. In pyrite, the distorted octahedral field may be expected to favor the population of the a_g orbital over the e_g orbitals since the S—Fe—S angle of 94·3° is greater than 90° for S atoms related by the threefold axis, thus increasing the mean distance between the ligands and electrons in the a_g orbital. This effect is indeed found to be significant. Both refinements (II) and (III) show considerable distortion from a spherical charge distribution towards the low-spin configuration with preference for population of the a_g orbital. The refined values of ζ, 3·79–3·93 a.u.$^{-1}$, correspond to a slightly contracted $3d$ shell compared with the optimized single Slater exponent of 3·73 a.u.$^{-1}$ calculated for an isolated iron atom by Clementi & Raimondi (1963).

The experimental deformation density about iron is plotted in Fig. 1 along with a plot of the model density corresponding to the parameters obtained from refinement (III). Both maps have been calculated including X-ray measurements with $I > 3\sigma(I)$ and include the smearing due to thermal motion of the atoms.

Rees & Mitschler (1976) have estimated the relative occupancies of the t_{2g} and e_g orbitals in the octahedral complex $Cr(CO)_6$ from the observed differences in the experimental density along the octahedral threefold and fourfold axes. Iwata (1977) has refined the populations of the a_g, e_g and e'_g orbitals using X-ray data from two compounds containing the nearly octahedral complexes, $[Co(NH_3)_6]$ and $[Co(NH_3)_6][Co(CN)_6]$. Her refinements, however, included only a portion of the X-ray data with all other parameters including the radial dependence of the density functions fixed.

Conclusion

With the expressions described here, orbital occupancies and estimated standard deviations can readily be obtained using existing aspherical refinement programs. Following the same approach, similar expressions can be derived from other site symmetries. This method can be expected to be useful as long as the effects of the crystal environment about the metal atom are primarily electrostatic and the covalent interactions are minor. A further limitation is imposed by the restricted form of the radial functions used in the analysis.

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A Discussion on Constrained Refinements

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Abstract

Three crystal structures are discussed in order to emphasize the difference between statistical and chemical or physical grounds of the different models used to represent crystal structure. The constrained models give an evident improvement over the unconstrained models for disordered crystal structures; they can also explain anomalies resulting at the end of the conventional refinement.

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