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Site Occupancy of the $PbWO_4$: Co and $PbMoO_4$: Co Systems

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In a previous investigation of Co-doped $PbWO_4$ and $PbMoO_4$, the EPR data were attributed to Co^{2+} ions occupying tetrahedral W (or Mo) sites of S_4 symmetry. Several years ago, Blasse proposed that the interstitial octahedral sites in scheelites could be occupied by U^{6+} ions. After reexamination of the g value and hyperfine-structure (hfs) data and from the $2D$ estimates, the case for interstitial site occupancy by Co^{2+} in these two scheelites can be made plausible. Although they are not conclusive, the optical data are compatible with this assignment.

In a previous EPR investigation of Co-doped $PbWO_4$, two of us (M.-C. Chen and J. O. Artman)[1] found this system to be characterized by an effective spin S of $\frac{1}{2}$ and the following spin-Hamiltonian parameters: $g_i = 4.50,\ 6.20,\ 2.07$; $|A_i| = 605,\ 970,\ 248$ MHz ($i = x,\ y,\ z$); $I = \frac{7}{2}$. The resonance evidently occurred in a ground doublet state; in addition it was not observable at temperatures above 20 K. A $2D$ value of $83\ \mathrm{cm}^{-1}$ was estimated from spin-lattice relaxation data. This D value was larger than those previously reported for Co^{2+} in tetrahedral sites; the hfs parameters were unusually large also. Nevertheless we attributed the EPR to Co^{2+} occupying tetrahedral fourfold coordinated W sites of S_4 symmetry. This assignment was influenced in part by some optical-absorption spectra available to us which consisted of a band at $16\,130\ \mathrm{cm}^{-1}$ and three weaker bands at 15150, 18180, and $19\,230\ \mathrm{cm}^{-1}$; we associated these sequentially with the ${}^4A_2 \rightarrow {}^4T_1\ ({}^4P)$ and the ${}^4A_2 \rightarrow {}^2E({}^2G)$, ${}^4A_2 \rightarrow {}^2T_1({}^2G)$ absorptions expected for Co^{2+} in a tetrahedral scheelite site. Correspondences with the results of extensive optical observations on Co-doped garnets[2] were also made.

Recently one of us (J.C.M.H.) proposed, as an alternative explanation, that these EPR data were due to Co^{2+} occupying sites of octahedral symmetry. Although interstitial octahedral sites occur in scheelites (of which $PbWO_4$ and $PbMoO_4$ are two examples) it has generally been assumed that $3d$, $4f$, and $5f$ dopants occupy the divalent metal site (or possibly the hexavalent metal site) substitutionally. However Blasse,[3] in an article on the fluorescence of uranium-activated compounds, proposed that U^{6+} ions in scheelites could occupy the interstitial octahedral sites. The nominal centers of these sites are situated midway between each pair of next-nearest W (or Mo) neighbors. The symmetry of the six nearest oxygens corresponds to a highly distorted octahedron; odd components would be expected in the crystal-field expansion.

Qualitative indications in favor of octahedral-site occupation are the large g and A anisotropies and the extremely large value of the zero-field splitting; these would seem to be incompatible with an orbital singlet ground state. Moreover, one of the g-tensor principal axes should be along the tetragonal crystal axis if Co^{2+} occupied a W site substitutionally without further reduction in symmetry. The absence of any simple geometrical relation between the g tensor and the crystal axes makes an assignment to a substitutional site somewhat unplausible.

The argument may be made more quantitative by examining the relations between the g and A components within the framework of the Abragam-Pryce theory.[4,5] For the octahedral case we have

$$g_x = \tfrac{1}{3}\,(10 + 4a - 4r) + k(1 + a - r) \equiv (g_s + kg_l^0)_x\ ,$$

$$g_y = \tfrac{1}{3}\,(10 + 4a + 4r) + k(1 + a + r) \equiv (g_s + kg_l^0)_y\ ,$$

$$g_z = \tfrac{1}{3}\,(10 - 8a) + k(1 - 2a) \equiv (g_s + kg_l^0)_z\ ,$$

where k is the orbital reduction factor and a and r are measures of the axial and rhombic fields, respectively:

$$a = 16A_2^0\langle r^2\rangle/315\lambda, \quad r = -4A_2^2\langle r^2\rangle/315\lambda\ .$$

In this formalism we disregard all of the levels of the ${}^4F$ term except those of the ground orbital triplet ${}^4T_1$. The ${}^4T_1$ splittings due to spin-orbit coupling $\lambda \vec{L} \cdot \vec{S}$, orthorhombic crystal field, and Zeeman energy are calculated under the assumptions $A_4^m = 0$ and $\lambda \gg A_2^0$, A_2^2. The hfs components are related to the g values through the formulas $A_i = P(g_{li}^0 - \frac{1}{2}\kappa g_{si})$, where P is a measure of $\langle r^{-3} \rangle$ and κ gives the unpaired s-electron admixture. We use values of P and κ identical to those found in hydrated Co salts,[4] 675 MHz and 0.325, respectively.

For the tetrahedral case the ground state is an orbital singlet $^4A_2$; we have simply $A_i = P[(g_i - 2) - \kappa]$, where the g_i refer to the "intrinsic" g values of the $^4A_2$ multiplet. (These intrinsic g values were found to be[1] 2.82, 2.52, and 2.10, respectively.) In this case the orbital contribution $P(g - 2)$ and the core polarization $P\kappa$ tend to compensate; we therefore expect lower hfs values for the tetrahedral case.

If we assume that the Co^{2+} ion is situated on an octahedral site, we find $k = 0.92$, $a = 0.485$, $r = 0.378$, and A_i values of 366, 765, and − 205 MHz, respectively. On the other hand if the Co^{2+} ion is assumed to be on a tetrahedral site, we have $A_i = 334$, 132, and − 152 MHz. We see that the A_i values calculated on the basis of octahedral-site occupancy appear to be the more reasonable ones. (The EPR experiments do not distinguish between positive and negative A_i values.) For octahedrally coordinated Co^{2+}, Gladney[6] has reported the following parameters in the $MgF_2:Co^{2+}$ case: $g_i = 6.03$, 2.30, 4.24; $A_i = 637$, 123, 210 MHz. Gladney[6] cites similar data for $ZnF_2:Co^{2+}$, $TiO_2:Co^{2+}$, and $NaF:Co^{2+}$. For octahedral Co^{2+} in YGaG, $g_\parallel$ and $g_\perp$ values of 7.027 and 2.665, respectively, were reported.[7] The hfs constants $|A|$ and $|B|$ were 922 and 45 MHz, respectively. Such values indeed are comparable to our data.

As we had mentioned earlier, our estimated $2D$ value of 83 cm^{-1} is unusually large for tetrahedrally coordinated Co^{2+} ($^4A_2$ ground state). A recent EPR study[7] of tetrahedrally coordinated Co^{2+} in YGaG did yield a $2D$ value of − 36 cm^{-1}, $g_\parallel$ and $g_\perp$ values of 2.42 and 2.19, respectively, and hfs constants less than 120 MHz in value. Tetrahedral site Co^{2+} $2D$ values of − 8.60 and − 10.7 cm^{-1} have been reported in $CoCs_3Cl_5$ and $CoCs_3Br_5$, respectively.[8] The g values cited were about 2.4, the hfs constants did not exceed 100 MHz.[9]

Clearly, from the aspect of the hfs splittings the data for tetrahedral Co^{2+} (Refs. 7–9) do not correspond too well to ours. (It should also be noted that the EPR spectra for tetrahedral Co^{2+} were all observable at temperatures up to 77 K at least.) On the other hand, fluorescence studies in the octahedral $MgF:Co^{2+}$ system[10] have indicated that the lowest excited state is 152 cm^{-1} above the ground state, which is not too far from our estimate of 83 cm^{-1}.

Evidence for site occupancy from the gross features of the $PbWO_4:Co$ optical-absorption data is still incomplete. Judging from Refs. 2, 7, 11, and 12 we would expect in the tetrahedral Co^{2+} case to see $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$, $^4T_1(^4F)$, $^4T_1(^4P)$ at 4500, 7000, 16 000 cm^{-1}, respectively. (The $^4A_2 \rightarrow {}^4T_2$ absorption would be relatively weak.) In the octahedral Co^{2+} case, we would expect (Refs. 2, 13, 14) to see $^4T_1(^4F) \rightarrow {}^4T_2(^4F)$, $^4A_2(^4F)$, $^4T_1(^4P)$ at 7500, 18 000, and 20 000 cm^{-1}, respectively. (The $^4T_1 \rightarrow {}^4A_2$ transition is relatively weak.) We had previously reported[1] observation of a band at 16 130 cm^{-1}. Upon reexamination at room and liquid-nitrogen temperatures of some Co-doped $PbWO_4$ and $PbMoO_4$ samples, we have found an additional band centered at 4400 cm^{-1}. No absorption was found in the 7000-cm^{-1} region.

The band at 16 130 cm^{-1} can be attributed equally well to $^4T_1(^4F) \rightarrow {}^4T_1(^4P)$ of octahedral Co^{2+} or, as was done in our earlier work,[1] to $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ of tetrahedral Co^{2+}. The absence of any absorption in the 7000-cm^{-1} region, however, suggests assignment of the relatively strong 4400-cm^{-1} band to the $^4T_1(^4F) \rightarrow {}^4T_2(^4F)$ transition of octahedrally coordinated Co^{2+}. Our spectra closely resemble those of $CoWO_4$,[13] in which Co^{2+} occupies a significantly distorted octahedral site with symmetry C_2. The value of Dq may be obtained by comparing our spectral data with the crystal-field calculations of Ferguson, Wood, and Knox.[13] We find a Dq value of 500 ± 50 cm^{-1}. This Dq value represents a reduction of about 35% from those commonly listed[13] for Co^{2+} at regular octahedral sites. This may not be astonishing when we remember that this scheelite interstitial site has two positively charged W^{4+} (Mo^{4+}) ions nearby.

In summary, from examination of the g value and hfs data and from the $2D$ estimates, the case for interstitial octahedral-site occupancy for the $PbWO_4:Co^{2+}$ and $PbMoO_4:Co^{2+}$ systems can be made plausible. Although they are not conclusive, the optical data are compatible with this assignment.

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Electron-Phonon Interaction in Transition Metals

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We point out that an expression for the electron-phonon matrix element in transition metals recently derived by Barisic, Labbé, and Friedel from a "Hubbard-Hamiltonian" formulation, and of particular interest in understanding the superconducting properties of these materials, follows from the more basic "modified-tight-binding" approximation of Fröhlich and Mitra.

In a recent publication Barisic, Labbé, and Friedel[1] have indicated that the order of magnitude of the electron-phonon interaction required to explain the superconducting properties of transition metals can be obtained by considering the electron-phonon coupling between d-band states. Barisic *et al.* have used a Hubbard-Hamiltonian formulation in which the electron-phonon coupling arises from the dependence on interatomic distance of a "hopping" or overlap integral as encountered in tight-binding band theory. Here we wish to point out that their expression for the electron-phonon interaction is not limited to the Hubbard-Hamiltonian model, but rather follows from the assumption that the electron wave function rigidly follows the motion of the ions, an assumption in the spirit of the tight-binding approximation. In particular, their result for the electron-phonon matrix element can be rederived by considering instead the matrix elements of the electron-phonon operator between modified-tight-binding wave functions as introduced by Fröhlich[2] and used by Mitra.[3]

Fröhlich's assumption is that the tight-binding wave function corresponding to the ions in static-displaced positions a distance $\vec{X}_\mu$ from their equilibrium-lattice positions $\vec{R}_\mu$ can be written in a modified-tight-binding form

$$\psi(\vec{r}) = \sum\nolimits_\mu e^{i\vec{k}\cdot\vec{R}_\mu}\,\phi(\vec{r}-\vec{R}_\mu-\vec{X}_\mu)\,, \tag{1}$$

where $\phi(\vec{r})$ is the localized orbital from which the tight-binding band arises. Using the Born-Oppenheimer formulation of the electron-phonon interaction leads to the electron-phonon matrix element [Eq. (2.18) of Ref. 3]

$$g^{\nu}_{kq} = M_1 + M_2\,, \tag{2}$$

where

$$M_2 = i\left(\frac{\hbar}{2MN\omega^0_{q\nu}}\right)^{1/2} \times \vec{\epsilon}^{\,\nu}_q \cdot \sum_{\vec{u}} \nabla J(\vec{u})\,[\sin\vec{k}\cdot\vec{u} - \sin(\vec{k}+\vec{q})\cdot\vec{u}\,] \tag{3}$$

in the notation of Ref. 1. Here M_1 involves degenerate three-center integrals, ignored by Barisic *et al.* (We note that these terms are not obviously negligible, since in the Garland-Bennemann[4] theory of the electron-phonon interaction they yield the principal contribution, although it should be noted that the latter have employed the Bloch rather than the Born-Oppenheimer viewpoint.)

Applying Eq. (3) to the case considered by Barisic *et al.*, in which the near-neighbor environment is orthorhombic, and using the expression of Ref. 1 for ∇J, we obtain

$$g^{\nu}_{kq} \cong M_2 = 2iq_0\left(\frac{\hbar}{2NM\omega^0_{q\nu}}\right)^{1/2} \times \sum_{\alpha} J(\vec{a}_\alpha)\,\frac{\vec{a}_\alpha\cdot\vec{\epsilon}^{\,\nu}_q}{a_\alpha}\,[\sin k_\alpha a_\alpha - \sin(\vec{k}+\vec{q}\,)_\alpha a_\alpha\,]\,, \tag{4}$$

which is just the result of Barisic *et al.* [see Eq. (6) of Ref. 1].

In conclusion we note that this more basic foundation for the electron-phonon matrix element to some extent reinforces the validity of the Barisic *et al.* calculation, and also indicates clearly its extension to a more realistic, degenerate d-band case.

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