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Covalency and orbit–lattice coupling

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Abstract. It is shown that in a covalent complex the values of the orbit–lattice interaction matrix elements are dominated by electron transfer and overlap effects, so that the current crystal field modulation model is inadequate for such complexes.

This is demonstrated by means of a sample calculation on a small molecule, and it is shown how the 'exact' dynamic effects should be evaluated within the framework of molecular orbital theory.

1. Introduction

The effects and mechanisms of the interaction of paramagnetic ions or 'centres' with the vibrations of the lattice in which they are embedded have received increasing attention, especially in very recent years.

Such interactions—the spin–lattice interaction or the orbit–lattice coupling—are not only related to specifically dynamic effects such as spin–lattice relaxation (Van Vleck 1939, 1940, 1941, Manenkov and Orbach 1966) and the Jahn–Teller effect (Ham 1965, 1968, Sturge 1967), but are also important for the understanding of static phenomena, such as the hyperfine and extrahyperfine structure of epr temperature dependance (Simanek and Huang 1966, Simanek and Orbach 1966, Shrivastava 1969, Huang *et al.* 1967), the associated effect of paramagnetic shifts of nuclear resonance (Shrivastava 1970), the effect of applied stress on epr spectra (Zdansky 1967, Sroubek *et al.* 1968, Calvo *et al.* 1969) and the intensities of electronically forbidden but vibronically allowed optical transitions in crystals (Ballhausen 1962).

The theory of such interaction within the limits of the crystal field theory is fairly well known, and the above mentioned references, as well as other recent papers (Weissfloch 1968, Bates 1967) concern themselves particularly with some of the modifications to be introduced in this theory to take account of a certain degree of delocalization of the electrons of the 'centre' onto the surrounding 'ligand' atom cores, and the 'hybridization' of central atom wavefunctions, to take 'covalence' into account.

Within the framework of the crystal field theory an atom in a given electron configuration is placed in a field due to the presence of the ligands. This field can be described by means of an effective one-electron operator. In the simplest approach this field is a Coulomb point charge potential for each ligand, but more generally it is developed in a series of Tesseral harmonics of the electron coordinates, and the coefficients—the crystal field parameters—are used as phenomenological adjustable parameters. Far beyond the point charge model, the theoretical calculation of the crystal field parameters may be quite sophisticated (Ellis and Newman 1967), and contain corrections to account for covalency, by prescribing the wavefunction of the electrons to be orthogonal to the ligand electrons' wavefunction (overlap correction) and by admitting a certain degree of configuration interaction (charge transfer). In this form the crystal field theory is able to account well for the behaviour of transition metal and rare earth ions in nearly ionic molecular clusters. In that case, $\mathscr{H}_{ol}$, the orbit–lattice interaction Hamiltonian is equally an effective one-electron operator, describing the variation of the potential energy operator (crystal field parameters) upon distortion of the complex (Curtis *et al.* 1969).

However, if covalency is quantitatively important, the basic assumptions of crystal field theory cease to be valid; the concept of an atom perturbed by its neighbours is inapplicable as a basis for a perturbation calculation, and configuration interaction becomes meaningless because there is no longer an atomic electron configuration as an adequate zero order starting point; we are thus in the province of molecular orbital theory. Here, the mixing coefficients between the atomic functions of different atoms in the cluster (if we limit ourselves to the LCAO approximation) are the result of a self consistent field calculation (Fenske and Radtke 1968), where a population analysis determines the effective charge distribution over the complex or cluster. In this approach, the Hamiltonian to be diagonalized is expressed on the basis of a number of atomic functions belonging to the different centres, and contains also a 'crystal field' part, describing the action of the average charge distribution of the ligands on the central atom orbitals, and reciprocally, that of the charge of the central atom and the other ligands on the orbitals of a given ligand. But since this charge is codetermined by the distribution of all the electrons in the cluster this effective crystal field is not a one electron operator, but part of a self consistent Hamiltonian, and may not satisfy the superposition principle. In this paper we wish to examine whether this effective crystal field is still able to represent an adequate starting point for the calculation of orbit–lattice interactions. That is, to ascertain whether the physically attractive and simple model of a 'vibrational modulation of the crystal field' can account for the essential part of the orbit–lattice interactions even if corrections should have to be applied to account for covalency. The result of our study is, as shall be seen, that such a model is inadequate when covalency is important, that it underestimates matrix elements of $\mathscr{H}_{ol}$ which are important numerically, and that it may not even render the correct sign of the matrix elements.

2. The orbit–lattice Hamiltonian in the molecular orbital model

The system formed by the paramagnetic 'central' atom (or of the molecular cluster of which it is a part) and the lattice is usually described by a Hamiltonian operator,

$$\mathscr{H} = \mathscr{H}_o + \mathscr{H}_{ol} = \mathscr{H}_e(q = 0) + \mathscr{H}_{vib} + \mathscr{H}_{ol}. \tag{1}$$

In this Hamiltonian, $\mathscr{H}_e(q = 0)$ is the static electronic Hamiltonian, including kinetic energy and interelectronic repulsions, and the potential energy of the electrons in the field of the neighbouring atomic cores ('crystal field') at the equilibrium position of the cluster, molecule or crystal. q is a generalized displacement coordinate which we shall use later. $\mathscr{H}_e$ also includes magnetic effects such as spin–orbit coupling, and may include the effect of externally applied fields. $\mathscr{H}_{vib}$ is the vibrational energy of the crystal lattice.

In what follows we shall assume the validity of the Born–Oppenheimer approximation (Huang *et al.* 1967). Let ϕ_{j0} be the solutions of the eigenvalue problem

$$\mathscr{H}_e(q = 0)\,\phi_{j0} = E_j^0 \phi_{j0}. \tag{2}$$

The wavefunctions ϕ_{j0} are, generally speaking, molecular orbitals, for which we shall later use the LCAO approximation. For a different configuration of the cluster ($q \neq 0$) we may write, similarly,

$$\mathscr{H}_e(q)\phi_{jq} = E_j^q \phi_{jq}. \tag{3}$$

q is not an operator but a parameter on which $\mathscr{H}_e(q)$ as well as E_j^q and the ϕ_{jq} depend.

$\mathscr{H}_{ol}$ is the interaction between the nuclear and electronic motions. Generally, $\mathscr{H}_{ol}$ is considered as a perturbation upon the undistorted wavefunctions

$$\Phi_j = \phi_{j0}\chi_{vib} \tag{4}$$

where χ_{vib} represents an eigenfunction of $\mathscr{H}_{vib}$. Physically, $\mathscr{H}_{ol}$ represents the change in electronic energy when the lattice vibrates or is otherwise distorted: that is, as an operator

$$\mathscr{H}_{ol} = \mathscr{H}_e(q) - \mathscr{H}_e(0). \tag{5}$$

It is convenient to decompose the general displacement q in terms of the normal coordinates of the lattice. Furthermore $\mathscr{H}_{ol}$ is usually expressed as a power series expansion in the displacement. Thus,

$$\mathscr{H}_{ol} = \sum_{\Gamma\gamma} \mathscr{H}_{ol}(\Gamma\gamma) = \sum_{\Gamma\gamma} \left(\frac{\partial \mathscr{H}_e}{\partial e(\Gamma\gamma)}\right)_0 e(\Gamma\gamma) + \text{higher order terms} \tag{6}$$

where $e(\Gamma\gamma)$ is a normal coordinate transforming as the component γ of the irreducible representation Γ of the symmetry group of the site. The reduced matrix elements of $(\partial \mathscr{H}_e/\partial_e(\Gamma\gamma))_0$ with wavefunctions $|\Gamma_i\gamma_i\rangle$ and $|\Gamma_j\gamma_j\rangle$ are the 'orbit–lattice coefficients' $G_\Gamma(\Gamma_i\Gamma_j)$ generally used to express experimental results.

Within the framework of crystal-field theory, the calculation of the matrix elements of $\mathscr{H}_{ol}$ between the wavefunctions ϕ_{i0} is quite straightforward. $\mathscr{H}_{ol}$ is given by the variation of the crystal field upon distortion, the zero order wavefunctions being atomic functions of the central atom.

$$\mathscr{H}_{ol}^{cf} = \sum_{\Gamma\gamma} \left(\frac{\partial v}{\partial e(\Gamma\gamma)}\right)_0 e(\Gamma\gamma) + \text{higher order terms} \tag{7}$$

In molecular orbital theory, it is not only the crystal field mentioned above that changes upon distortion of the cluster, since the selfconsistency of the charge distribution over the cluster is maintained. There are other effects which produce a change in the electron density over the whole cluster, thus changing the wavefunction and the energy in a subtle and profound manner. This change is not readily estimated, and, in principle, calls for a complete selfconsistent molecular orbital calculation for each atomic configuration.

Such a geometry dependent molecular orbital calculation yields a selfconsistent Hamiltonian matrix expressed in the basis $\{u_\mu\}$ of the atomic wavefunctions out of which the LCAO are constructed. The matrix element of $\mathscr{H}_{ol}$ is then given as the scalar product of $\delta\mathscr{H}_{\mu\nu} = \mathscr{H}_{\mu\nu}(q) - \mathscr{H}_{\mu\nu}(0)$ with the vectors $|i\rangle = \Sigma_\mu c_\mu^i u_\mu$ and $|j\rangle = \Sigma_\nu c_\nu^j u_\nu$ which are the eigenfunctions of $\mathscr{H}_{\mu\nu}(0)$:

$$\sum_\mu (\mathscr{H}_{\mu\nu}(0) - E_j^0 \mathscr{S}_{\mu\nu}(0))\, c_\mu^j = 0 \tag{8}$$

where $\mathscr{S}_{\mu\nu} = \langle u_\mu | u_\nu \rangle$ is the overlap matrix. Thus

$$\langle i | \mathscr{H}_{ol} | j \rangle = \sum_{\mu\nu} (\mathscr{H}_{\mu\nu}(q) - \mathscr{H}_{\mu\nu}(0))\, c_\mu^i c_\nu^j. \tag{9}$$

It is easy to show that the effect of distortion, which in the above treatment is put into the expression of the Hamiltonian matrix, may equally be expressed by means of the distorted wavefunctions, in its most general form, if

$$\phi_j^q = \phi_j^0 + \delta\phi_j \simeq \phi_j^0 + \left(\frac{\partial \phi_j^0}{\partial e(\Gamma\gamma)}\right)_0 e(\Gamma\gamma) \tag{10}$$

then

$$\langle i | \mathscr{H}_{ol} | j \rangle = -E_i^0 \langle \delta\phi_j | \phi_i^0 \rangle - E_j^0 \langle \phi_j^0 | \delta\phi_i \rangle. \tag{11}$$

Expressions equivalent to equation (10) have been used to express the phonon-induced changes in the wavefunctions (Simanek and Huang 1966, Shrivastava 1970). If the effect of covalency is introduced by requiring that the modified central atom orbitals be orthogonal to the ligands, as is frequently done for nearly ionic clusters, one should required that such orthogonality be invariant upon distortion or vibration. The changes obtained for the MO coefficients, δc_μ^i, are then proportional to the corresponding changes in the overlap integrals, and the results obtained for $\langle i | \mathscr{H}_{ol} | j \rangle$ will be correct within the limitations of the model. However, great care must be exercised when the MO gradients of LCAO wavefunctions are obtained by means of 'complete' MO calculations, since then the atomic orbitals are

then not correctly given by the gradients of the coefficients, because the functions ϕ_j^q and ϕ_j^0 are not expressed in the same basis set, and equation (9) rather than equation (11) should be used in computations of $\mathscr{H}_{ol}$.

A complete orbit–lattice coupling calculation like that described above represents a rather forbidding task for a complex cluster with many normal modes. Since, furthermore, experimental data leading to the measurement of orbit–lattice coupling in strongly covalent clusters are very scarce, we preferred to perform such a calculation on a very simple linear triatomic molecule, $MnCl_2$, considered as an example of what might happen in a more complicated case. Such a molecule is obviously not a realistic model for a covalent crystal with a paramagnetic impurity, but the calculation reproduces all the features of that complex-ion cluster of the general type MX_n^{k-}, on which many molecular-orbital calculations have been performed (Balhausen and Gray 1965, Fenske and Radtke 1968). One should expect to obtain at least correct order-of-magnitude estimates for the effect of symmetric and assymmetric stretching and bending modes on a covalent cluster containing a d^5 transition metal ion.

3. Results and discussion of the sample calculation

The molecular orbital calculations on $MnCl_2$ were done by a semiempirical Hartree–Fock–Roothaan method, using the 3d, 4s and 4p functions of the central atom and the 3s and 3p functions of the ligands, and for several displacements of Σ_g^+, Σ_u^+ and Π_u symmetry and small amplitude, so that second order effects were neglible. The matrix elements of $\mathscr{H}_{ol}$ where obtained using equation (9), for the different bonding, antibonding and nonbonding levels, and for distortions according to the three normal modes possible in a linear triatomic molecule. These are the matrix elements which we call 'exact'. Besides the 'exact' matrix elements we have also calculated the matrix elements of the variation of the crystal field contribution to the semiempirical molecular Hamiltonian, in order to test the validity of the 'modulation of the crystal field' picture. A more detailed description of the calculation and numerical values are given for illustration in the appendix. The general trends of about 60 matrix elements which were computed lead to the conclusion that the crystal field modulation model for the dynamic and off-equilibrium properties of a covalent cluster is not more valid than is the crystal field model itself for the static and equilibrium properties.

(i) When allowed by symmetry, 'exact' matrix elements between functions which are not coupled by $\mathscr{H}_{lo}^{cf}$ have about the same size as those between functions which are.

(ii) For the assymmetric stretching mode, and for small displacements, the changes of the crystal field in the coulombic approximation is mostly due to second order terms of even parity. Therefore matrix elements of $\mathscr{H}_{lo}^{cf}$ between states of different parities are small. This restriction is not valid for the matrix elements of the 'exact' $\mathscr{H}_{ol}$.

As for the bending mode, the fact that the crystal field is especially ineffective for orbit–lattice interaction reflects its relative isotropy in this axial case, when a small ligand–ligand repulsion is neglected. This will not be true in a crystal, where no such 'pure' bending is possible on account of the neighbouring atoms in the lattice. In opposition to the softness of the crystal field against bending, the covalent molecule shows a great rigidity due to the strongly directional character of the covalent bond.

(iii) Among the different one-electron molecular orbitals there are some which are more 'covalent' than others: that is, the electron density distribution, as given by the different c_μ^j coefficients and overlap integrals, is more uniform over the whole molecule. Nevertheless the above trends do not distinguish such differences. This means that when covalency as an overall property of the cluster is important, the reshuffling of charge on any atom due to the general readjustment of the orbitals upon distortion is more important than the crystal field modulation.

Appendix 1. Electronic structure of $MnCl_2$ and orbit–lattice interaction

For the calculation of the Hamiltonian matrix in the atomic orbital basis and of the molecular coefficients, we use a basis of 17 atomic functions in combinations adapted

to $D_{\infty h}$ symmetry, as follows (no subscript refers to the metal, and subscripts 1 and 2 to the two chlorine atoms. The principal quantum number is omitted for simplicity; thus s = 4s (Mn); $z_1 = 3p_z$ (Cl_1), etc. The z axis is taken along the molecular axis, pointing towards atom 2; z_1 points towards 2 and z_2 towards 1; x_1, x and x_2 are arbitrary but all parallel to each other, and so are y_1, y and y_2.

We have

$$\sigma_g^+ = s;\ d_{z^2}:\frac{1}{\sqrt{2}}(s_1 + s_2);\ \frac{1}{\sqrt{2}}(z_1 + z_2)$$

$$\sigma_u^+ = z;\ \frac{1}{\sqrt{2}}(s_1 - s_2);\ \frac{1}{\sqrt{2}}(z_1 - z_2)$$

$$\pi_u = \left[x;\frac{1}{\sqrt{2}}(x_1 + x_2)\right];\left[y;\frac{1}{\sqrt{2}}(y_1 + y_2)\right]$$

$$\pi_g = \left[d_{xz};\frac{1}{\sqrt{2}}(x_1 - x_2)\right];\left[d_{yz};\frac{1}{\sqrt{2}}(y_1 - y_2)\right]$$

$$\delta_g = [d_{x^2-y^2}];[d_{xy}].$$

From these automatic functions we performed a semiempirical molecular orbital calculation using the method described elsewhere (Kandel *et al.* 1969, for several nuclear configurations. The ground state of the molecules is the sextet $^6\Sigma_g^+$ corresponding to the strong field configuration $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(1\pi_g)^4(1\pi_u)^4(\delta_g)^4(2\pi_g)^2(3\sigma_g^+)^1$ (the one-electron molecular orbitals are ordered by increasing energy).

Since we are not interested in the term energies of the excited states of the molecule, we did not calculate the complete electrostatic interaction matrix. The off diagonal matrix elements of $\mathscr{H}_{ol}$ and $\mathscr{H}_{ol}^{cf}$ can be obtained directly from the one-electron MO; these matrix elements for determinantal wavefunctions corresponding to the ground and excited states reduce to one-electron matrix elements, since the effective semiempirical Hamiltonian of our problem behaves as an one-electron Hamiltonian once selfconsistency is attainted for each nuclear configuration.

Therefore we limited ourselves to the calculation of $\langle i|\mathscr{H}_{ol}|j\rangle$ according to equation (9), using the coefficients c_μ^i obtained for the undistorted molecule, and $\mathscr{H}_{ol}$ for various distortions. In the semiempirical Hamiltonian the crystal field contribution to $\mathscr{H}_{\mu\nu}(q)$ appears explicitly; so, $\langle i|\mathscr{H}_{ol}^{cf}|j\rangle$ was obtained in the same manner as the 'exact' values $\langle i|\mathscr{H}_{ol}|j\rangle$, from the variation of the crystal field contribution.

Table 1. Numerical values of matrix elements of $\mathscr{H}_{ol}$ and $\mathscr{H}_{ol}^{cf}$ (units of 10^3 cm^{-1} a.u.$^{-1}$ for stretching and 10^3 cm^{-1} rad^{-1} for bending)

(i) Symmetric stretching

$\lvert i\rangle$	$\lvert j\rangle$	$\langle i\lvert\mathscr{H}_{ol}\rvert j\rangle$	$\langle i\lvert\mathscr{H}_{ol}^{cf}\rvert j\rangle$
$1\sigma_g^+$	$2\sigma_g^+$	0·726	5·792
$1\sigma_g^+$	$3\sigma_g^+$	10·410	2·080
$1\sigma_g^+$	$4\sigma_g^+$	46·240	16·410
$2\sigma_g^+$	$3\sigma_g^+$	5·736	15·820
$2\sigma_g^+$	$4\sigma_g^+$	−7·956	28·300
$3\sigma_g^+$	$4\sigma_g^+$	−15·422	−6·342
$1\sigma_u^+$	$2\sigma_u^+$	−15·016	8·684
$1\sigma_u^+$	$3\sigma_u^+$	38·930	−7·048
$2\sigma_u^+$	$3\sigma_u^+$	19·966	−7·624
$1\pi_u$	$2\pi_u$	1·156	−4·172
$1\pi_g$	$2\pi_g$	6·998	22·106

Table 1—*continued*

(ii) Assymetric stretching

$i\rangle$	$j\rangle$	$\langle i\|\mathscr{H}_{ol}\|j\rangle$	$\langle i\|\mathscr{H}_{ol}^{cf}\|j\rangle$
$1\pi_u$	$2\pi_u$	21·2625	−4·810
$1\pi_u$	$1\pi_g$	10·415	0
$1\pi_u$	$2\pi_g$	24·540	0
$2\pi_u$	$1\pi_g$	−9·300	0
$2\pi_u$	$2\pi_g$	9·395	0
$1\pi_g$	$2\pi_g$	−2·8375	17·8525
$1\sigma_g$	$2\sigma_g$	−4·710	−1·5525
$1\sigma_g$	$3\sigma_g$	1·0975	1·410
$1\sigma_g$	$4\sigma_g$	2·6575	8·4175
$1\sigma_g$	$1\sigma_u$	3·3525	0·0050
$1\sigma_g$	$2\sigma_u$	1·680	0·0180
$1\sigma_g$	$3\sigma_u$	−6·9625	0·245
$2\sigma_g$	$3\sigma_g$	−1·1875	3·610
$2\sigma_g$	$4\sigma_g$	−2·5350	13·5450
$2\sigma_g$	$1\sigma_u$	5·8600	0·0150
$2\sigma_g$	$2\sigma_u$	1·7325	0·0375
$2\sigma_g$	$3\sigma_u$	4·8800	−0·5175
$3\sigma_g$	$4\sigma_g$	2·5400	4·3100
$3\sigma_g$	$1\sigma_u$	4·6125	0·0200
$3\sigma_g$	$2\sigma_u$	6·4775	0·0475
$3\sigma_g$	$3\sigma_u$	1·2275	−0·6625
$4\sigma_g$	$1\sigma_u$	31·3625	0·0700
$4\sigma_g$	$2\sigma_u$	8·0475	0·1700
$4\sigma_g$	$3\sigma_u$	8·1450	2·2925
$1\sigma_u$	$2\sigma_u$	−7·1125	−3·5575
$1\sigma_u$	$3\sigma_u$	20·7475	3·5700
$2\sigma_u$	$3\sigma_u$	14·6825	−5·6150

(iii) Bending

$i\rangle$	$j\rangle$	$\langle i\|\mathscr{H}_{ol}\|j\rangle$	$\langle i\|\mathscr{H}_{ol}^{cf}\|j\rangle$
$1\sigma_g$	$2\sigma_g$	0·035	0·035
$1\sigma_g$	$3\sigma_g$	0·135	0·135
$1\sigma_g$	$4\sigma_g$	0·045	0·045
$1\sigma_g$	$1\pi_u$	13·0100	0·000
$1\sigma_g$	$2\pi_u$	49·0950	0·000
$2\sigma_g$	$3\sigma_g$	0·375	0·375
$2\sigma_g$	$4\sigma_g$	0·155	0·155
$2\sigma_g$	$1\pi_u$	−19·1050	0·000
$2\sigma_g$	$2\pi_u$	14·6300	0·000
$2\sigma_g$	δ_g	0	0
$3\sigma_g$	$4\sigma_g$	0·475	0·475
$3\sigma_g$	$1\pi_u$	−7·1450	0·000
$3\sigma_g$	$2\pi_u$	−10·0550	0·000
$3\sigma_g$	δ_g	0	0
$4\sigma_g$	$1\pi_u$	−103·7500	0·000
$4\sigma_g$	$2\pi_u$	68·9450	0·000
$4\sigma_g$	δ_g	0	0
$1\pi_u$	$2\pi_u$	0·700	0·700
$1\pi_u$	δ_g	−25·255	0·000
$2\pi_u$	δ_g	−4·985	0·000

Table 1 lists the matrix elements thus obtained. The distortion of Σ_g^+ symmetry does not change the symmetry of the molecule, and does not mix representations of $D_{\infty h}$. The assymetric stretching mode Σ_u^+ reduces symmetry to $C_{\infty v}$ and mixes the representations of g and u character. The bending mode leads to C_{2v} symmetry and produces mixing of σ_g^+ with $\pi_u(x)$ and $\delta_g(x^2 - y^2)$.

Obviously the actual values listed have only an indicative value and should only serve to illustrate the trends mentioned in the text.

Appendix 2. Molecular orbitals and energies for $MnCl_2$

	4s (Mn)	$3d_\sigma$ (*Mn*)	3s (Cl)	$3p_\sigma$ (Cl)	10^3 cm^{-1}
$1\sigma_g^+$	0·0887	0·0860	0·9451	−0·1562	−242·7
$2\sigma_g^+$	0·0928	0·2937	0·0045	0·8686	−140·1
$3\sigma_g^+$	−0·3267	0·9104	−0·0601	−0·2494	−94·4
$4\sigma_g^+$	1·1787	0·3740	−0·5947	−0·6953	56·3
	$4p_\sigma$ (Mn)	3s (Cl)	$3p_\sigma$ (Cl)		
$1\sigma_u^+$	−0·0309	0·9845	−0·1357		−240·2
$2\sigma_u^+$	−0·0761	0·1140	0·9799		−133·4
$3\sigma_u^+$	1·0254	0·2477	0·1900		−68·3
	$3d_\pi$ (Mn)	$3p_\pi$ (Cl)			
$1\pi_g$	0·3688	0·8899			−129·2
$2\pi_g$	0·9361	−0·4694			−96·9
	$4p_\pi$ (Mn)	$3p_\pi$ (Cl)			
$1\pi_u$	−0·0580	0·9904			−125·0
$2\pi_u$	1·0079	0·1955			−80·6
	3d (Mn) (n.b.)				
δ_g	δ				−106·7

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