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Sherwood, P.M.A.

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CRYSTAL-FIELD AND BAND-BROADENING EFFECTS
ON THE APPARENT 4d SPIN-ORBIT SPLITTING
IN CADMIUM PHOTOELECTRON SPECTRA*

P.M.A. Sherwood[†] and D. A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

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ABSTRACT

The apparent spin-orbit splitting of 4d energy levels in cadmium metal and cadmium dimethyl is discussed in terms of crystal-field and band-broadening models. The use of nuclear field gradients from Mössbauer and NQR measurements in distinguishing between these two models is evaluated by CNDO calculations on cadmium dimethyl and a cadmium atom cluster (Cd_{13}). The calculations suggest that the use of nuclear field gradients cannot reliably distinguish between crystal-field and band-broadening mechanisms.

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[†]Permanent address: Department of Inorganic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, England.

I. Introduction

There have been many studies of the apparent spin-orbit splitting of core and valence-level hole-states, as observed by photoelectron spectroscopy. For a number of cases¹⁻⁸ in which the d^9 configuration was produced in the photoelectron experiment, the apparent spin-orbit splitting was found to be greater than that of the free ion. This increase in apparent spin-orbit splitting has been interpreted using two different models, a "crystal-field" model and a "band-broadening", or "d band overlap" model. The two models differ primarily in that the crystal-field model assumes that lattice symmetry is dominant in increasing the apparent spin-orbit splitting, while the band-broadening model assumes that crystal symmetry has little influence.

In the crystal-field model the increase in apparent spin-orbit splitting is explained² by considering the final state of the photoelectric transition in terms of a one-electron (hole) problem, and writing the appropriate hole-state Hamiltonian in the one-electron approximation as:

$$\mathcal{H} = h_o + h_c + h_{so} \quad . \quad (1)$$

Here h_o contains the kinetic-energy operator and the spherical Coulomb potential of the inner ion core. The h_o term includes the potentials due to neighboring atomic cores and the valence electrons (including those of the atom under consideration), and h_{so} is the one-electron spin-orbit Hamiltonian. One may, for reasons discussed previously,² assume that direct changes in the expectation value of h_{so} cannot be

responsible for the increase in apparent spin-orbit splitting in the case of core-like levels. The increase is therefore explained by the term h_c , which may be written in terms of crystal-field parameters, B_k^q :

$$h_c = \sum_{k=2,4} \sum_{q=-k}^k B_k^q O_k^q \quad (2)$$

Here O_k^q is the appropriate spin operator,⁹ which may be expressed as eigenvalues of angular momentum operators; e.g.,

$$O_2^0 = 3L_z^2 - L(L+1) \quad (3)$$

For d electrons O_2^0 takes the value $(3L_z^2 - 6)$, giving for the D_{3h} case of cadmium dimethyl and cadmium metal,

$$h_c = 3B_2^0 (L_z^2 - 2) \quad (4)$$

if the small B_4^0 term is neglected. There are many other ways of defining the crystal-field parameters, some using different symbols for the same term (e.g., Bancroft et al.,⁸ call B_2^0 , C_2^0 which both take the same value), and some the same symbol for different terms. All the crystal-field parameters of a given k and q are proportional to one another. Using this approach Ley et al.² obtained a value of B_2^0 of -0.117 eV for the crystal-field parameter that explained the apparent spin-orbit splitting in cadmium metal, and Bancroft et al.⁸ a value of B_2^0 of -0.026 eV for the crystal-field parameter that explained the apparent spin-orbit splitting in cadmium dimethyl.

In the band-broadening, or overlap, model the increase in apparent spin-orbit splitting is explained^{2,3,5} by direct changes in the expectation value of h_{so} due to renormalization of the d electron wavefunction

via its orthogonalization to wavefunctions on neighboring atoms. Orthogonalization leads to an increase in the d electron wavefunction coefficient, and therefore in the coupling strength ξ . This effect is overlap-dependent, and the same overlap will also determine the extent to which an atomic level is broadened into a band. It has therefore been argued² that the overlap model is not important in the increase of apparent spin-orbit splitting in core-like levels.

A number of experimental studies have been carried out to determine which of the two models is more important in explaining the observed effects. Shevchik³ examined the x-ray photoelectron spectrum of Au-Cd alloys made by co-sputtering the constituents. He found no evidence for an enhancement of the spin-orbit splitting of the Au 5d level due to the Cd crystal field. Further he found that the apparent spin-orbit splitting of the Au 5d doublet was linearly dependent upon the Au concentration. He interpreted these results as supporting the band-broadening model. However this does not invalidate the crystal-field model, because the Au 5d bands, which are 5 eV wide and 2-7 eV below the Fermi level, are valence-like, in contrast to the core-like Cd 4d level, which is 1 eV wide and some 10 eV below the Fermi level. It has also been pointed out⁷ that one would expect less Au-Cd overlap than Cd-Cd overlap. A similar result was observed for the Ag-In⁷ alloy system for the variation of apparent spin-orbit splitting in the valence-like Ag 4d band. Studies on the core-like Cd 4d level in the Ag-Cd alloy system⁷ could not distinguish between the two models. The net result of these experimental studies on alloys is that either model

is still a suitable candidate for explaining the enhanced splitting in core-like levels.

Bancroft et al.⁸ attempted to distinguish between the two models by comparing the crystal-field parameters for cadmium metal and cadmium dimethyl (vide supra) with nuclear electric field gradients obtained from Mössbauer and NQR measurements. Their high resolution HeI photoelectron spectrum of cadmium dimethyl showed five peaks in the Cd 4d level region which can be unambiguously explained by the crystal-field model. The results for cadmium metal² were obtained by x-ray photoelectron spectroscopy and the lower resolution led to two partially-resolved peaks. A term of B_2^0 symmetry in the crystal field is known¹⁰ to interact directly with the nuclear electric quadrupole moment and with the p electrons, and this interaction creates a proportional electric field gradient at the nucleus (q^n). Under certain conditions B_2^0 could be assumed proportional to the electric field gradient due to the valence electrons (q^v). Bancroft et al.⁸ assumed that q^v could be replaced by q^e , an effective electric field gradient at the 4d electronic site. For two substances A and B they assumed:

$$\frac{|B_2^0|_A}{|B_2^0|_B} = \frac{q_A^e \langle F^2 \rangle_A}{q_B^e \langle F^2 \rangle_B} \quad (5)$$

where $\langle F^2 \rangle$ are the quadrupole overlap parameters.¹¹ Using this expression, and assuming $q_A^e/q_B^e = q_A^n/q_B^n$, they obtained good agreement between the ratio of B_2^0 values and the ratio of q^n values obtained experimentally multiplied by a ratio of estimated quadrupole overlap parameters for the similar compounds cadmium dimethyl and $(CH_3)_2Sn$ (dibenzoylmethane

anion)₂. They then applied a similar procedure to estimate the B_2^0 parameter for cadmium (a very different type of material) using their value of -0.026 eV for cadmium dimethyl and the $e^2 q_A^n q_B^n$ values for cadmium metal¹² (125.0 MHz) and cadmium dimethyl¹² (946 MHz). Upon substitution into equation (5), with the ratio of the quadrupole overlap parameters set at unity, B_2^0 for cadmium metal was estimated as -0.0034 eV. Taking this value of B_2^0 for cadmium metal rather than the value of -0.117 eV obtained by Ley et al.² we obtain by fitting to a calculated² plot of energy vs. B_2^0 an apparent spin-orbit splitting of only 0.04 eV greater than that of the free ion. Bancroft et al.⁸ therefore concluded that the apparent spin-orbit splitting in metallic cadmium must be explained by the band-broadening mechanism.

We believe that this does not close the matter, because the use of equation (5) is approximate at best. In fact it appears to be based on the misconceptions that all interactions can be treated in a point-charge approximation and that the 4d shell, like the nucleus, is so small that it can be treated like a point multipole moment interacting with the electromagnetic field. However, it was pointed out earlier² that the analogy between the electric field gradient at the nucleus and the enhanced spin-orbit splitting rests upon a similarity in symmetry properties; the matrix elements involved in these different phenomena are of course quite different, and not necessarily proportional. In particular the approximation that q_A^e/q_B^e equals q_A^n/q_B^n can only be expected to hold if the bonding configurations in A and B are simple and very similar. One might well expect this to be the case for the two organometallic compounds studied by Bancroft et al.⁸ However

cadmium metal and cadmium dimethyl would be expected to show significant differences in the valence shell, and the argument of Bancroft et al. against the crystal-field model is incorrect.

Of course it might be possible that Equation (5) would be correct by accident. In order to test this question and better understand the valence shells of cadmium metal and cadmium dimethyl, we have carried out CNDO calculations on $\text{Cd}(\text{CH}_3)_2$ and on a metal atom cluster Cd_{13} . The results of these calculations show that the use of Equation (5) is in fact inappropriate for these two compounds, and that the crystal-field model is probably a suitable model for cadmium metal.

II. Calculations and Discussion

Calculations were carried out using the CNDO program described previously.¹³ The diagonal core Hamiltonian matrix elements, $(I + A)/2$, and the bonding parameters β_A^0 were those used for CNDO/2 calculations¹⁴ on the elements C and H. The $(I + A)/2$ values for cadmium were obtained using an I value from atomic data,¹⁵ and A values from the estimated A_p value of Ginsberg and Miller¹⁶ and atomic data,¹⁵ giving 15.0342 (Cd 4d), 6.5636 (Cd 5s), and 2.0669 (Cd 5p), all in electron volts. The β_4^0 values for cadmium were obtained using the relation of Santry and Segal¹⁷ for relating bonding parameters for second row elements to those of first row elements, giving the values 17.8073 eV (4d) and 33.0246 eV (5s/p). Slater exponents were used for C and H and Burns¹⁸ exponents were used for cadmium. The calculations were carried out on a CDC 7600 computer, using CDC single precision, and iterations were stopped when the electronic energy converged to 10^{-6} . In the Cd_{13}

the initial electronic energy levels had to be populated such that the symmetry of the system was not artificially lowered. This situation can arise in the Cd_{13} cluster due to the very close stacking of the energy levels into a band.

To compare the results for cadmium dimethyl and cadmium metal we had to choose an approach appropriate to both. Normally cadmium dimethyl would be considered using a molecular orbital approach and cadmium metal using a band structure approach. The evaluation of crystal field parameters B_2^0 requires the identification of a specific number of energy levels (for the D_{3h} case of cadmium dimethyl and cadmium metal there will be three 4d cadmium levels, two doublets and one singlet). In the metallic cadmium three (A'_1 , E' , and E'') identifiable levels will be found at $\vec{k} = 0$. If there is appreciable energy dispersion with wave vector $\vec{k}$ leading to band broadening, then the situation will be complex, with the band being made up of A' , and E' , and E'' levels admixed throughout the band (e.g., A'_1 , E' , A'_1 , E'' , E'' , A'_1 , E' , etc.) with Bloch functions that are $\vec{k}$ -dependent linear combinations of A'_1 , E' , and E'' . In a band theory calculation we may still identify projections of the density of states of a particular symmetry type, but clearly for such a case it will not be possible to evaluate crystal-field parameters. Thus the test of applicability of the crystal-field model to cadmium metal is whether energy dispersion with wave vector can be neglected, i.e., whether the 4d level is core-like or not.

We have applied the CNDO molecular orbital method to both cadmium dimethyl and to cadmium metal so that values calculated may be compared

more reliably by using the same method of calculation. Though this method of calculation is very approximate we may expect some of the errors of approximation to be eliminated if we evaluate a ratio of two quantities calculated by this method. Cadmium dimethyl was taken as a molecule with a linear C-Cd-C unit with a Cd-C distance of 211.2pm^{19} and the methyl groups in the eclipsed position. The C-H bondlength was assumed to be 109.3pm and the H-C-H and H-C-Cd angles were assumed to be $109^\circ 40'$. For cadmium metal we chose the smallest fragment of the cadmium metal lattice which reflected the symmetry of the lattice. Thus the Cd_{13} cluster chosen has a central atom that has the hcp symmetry of the metal lattice in its nearest neighbors. The Cd-Cd distance and geometry of the cluster were taken to be the same as that of the bulk metal.²⁰

The results for cadmium dimethyl show three closely-spaced levels (two doublets and a singlet) that are almost entirely Cd 4d in character, with almost no bonding interaction between the Cd 4d orbitals and the methyl groups. The d orbital sequence is $\sigma > \pi > \delta$. In terms of the crystal-field parameters⁹ these orbitals should have energies (except for a constant factor) $(-6B_2^0 + 72B_4^0) > (-3B_2^0 - 48B_4^0) > (6B_2^0 + 12B_4^0)$. Using these values we obtain the crystal-field parameters $B_2^0 = -0.0429\text{ eV}$ and $B_4^0 = 0.0020\text{ eV}$ (with the appropriate sign change on going from d^1 to d^9). These values are in reasonable agreement with Bancroft et al.⁸ who find B_4^0 negligible and $B_2^0 = -0.026\text{ eV}$. The calculation also shows that the main bonding interaction between Cd and the methyl groups is through $p\pi$ orbitals (involving Cd 5p electrons) and $p\sigma$ orbitals (involving Cd 5p and 5s electrons), and as expected these

orbitals have a lower binding energy than the Cd 4d orbitals. Also as expected, cadmium dimethyl is found to be very covalent with a cadmium charge of -0.1695, a carbon charge of -0.1689, and a hydrogen charge of 0.0842.

The results for the cadmium cluster (Cd_{13}) show at the lowest binding energies a number of widely-spaced and partly empty levels involving Cd 5s and Cd 5p orbitals. We consider these to be the equivalent of the s-like conduction bands of the bulk metal.^{1,21} Some 5 eV below the bottom of this set of levels are 65 orbitals that have almost entirely Cd 4d orbital character. These orbitals spread over an energy range of 1.5401 eV. Nearly all the central metal atom d character (86%) is concentrated into four orbitals near the bottom of the Cd 4d orbitals. These four orbitals lie, in order of decreasing binding energy, at: $A'_1(1.7) > E'(3.3) > E''(0.8) > E''(2.9)$, where the number in parenthesis refers to the number of central metal atom Cd 4d electrons in the orbital(s). The fact that we find four energy levels with significant central metal atom 4d character implies that some band-broadening has taken place (vide supra); however, if we ignore the $E''(0.8)$ level, then some 80% central metal character stills falls into three orbitals, A'_1 , E' , and E'' . We may use these three orbitals to obtain crystal field parameters $B_2^0 = 0.0220$ eV and $B_4^0 = 0.0012$ eV (with the appropriate sign change on going from d^1 to d^9). These values are not in very good agreement with the results of Ley et al.² who found B_4^0 negligible and $B_2^0 = -0.117$ eV. The B_4^0 value is satisfactory, but the B_2^0 value of the calculation is five times smaller than Ley et al.² obtained. It is, however, also six times larger than

Bancroft et al.⁸ predicted (vide supra). At some point it is no longer worthwhile to pursue an approximate calculation such as CNDO, but we note that the calculation implies that band-broadening effects are sufficiently small to allow a crystal-field model to be applied. The Cd_{13} cluster has three types of cadmium atom that differ due to the symmetry of the cluster. This is reflected in the calculated cadmium atom charges. The central atom has a charge of 0.1857, the hexagon of cadmium atoms surrounding it a charge of -0.0375 each, and the triangle of cadmium atoms above and below the central atom a charge of 0.0066 each. In the bulk metal the cadmium atoms will all have zero charge, of course. The difference in our model between the central atom of the cluster and the other atoms may cause its energy levels to be forced together at the bottom of the band, so reducing B_2^0 artificially.

There is another, more compelling reason to expect that the B_2^0 value estimated above to be too small. Electronic relaxation toward the final Cd 4d hole state in the photoelectric transition will amplify the electronic contributions to B_2^0 , while the contributions from the positive ion cores will be unaffected if the Born-Oppenheimer condition holds. Thus the total effective B_2^0 will be enhanced if the electronic component is dominant in the ground state (which is true in this case) and decreased or changed in sign otherwise.

To test the accuracy of the substitution of $q_A^e/q_B^e = q_A^n/q_B^n$ in Equation (5) we can calculate $q^n(\text{Cd}(\text{CH}_3)_2)/q^n(\text{Cd}_{13})$ and compare it with our calculated $B_2^0(\text{Cd}(\text{CH}_3)_2)/B_2^0(\text{Cd}_{13})$ value. We use the expression:²²

orbitals have a lower binding energy than the Cd 4d orbitals. Also as expected, cadmium dimethyl is found to be very covalent with a cadmium charge of -0.1695, a carbon charge of -0.1689, and a hydrogen charge of 0.0842.

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To test the accuracy of the substitution of $q_A^e/q_B^e = q_A^n/q_B^n$ in Equation (5) we can calculate $q^n(\text{Cd}(\text{CH}_3)_2)/q^n(\text{Cd}_{13})$ and compare it with our calculated $B_2^0(\text{Cd}(\text{CH}_3)_2)/B_2^0(\text{Cd}_{13})$ value. We use the expression:²²

$$C = C_0 \left(P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right) \quad (6)$$

where C is the nuclear quadrupole coupling constant, P_{zz} , P_{xx} , and P_{yy} the electron populations of the P_z , P_x , and P_y atomic orbitals, respectively, and C_0 is the nuclear quadrupole coupling constant per p electron.

We thus obtain:

$$\frac{q^n(\text{Cd}(\text{CH}_3)_2)}{q^n(\text{Cd}_{13})} = \frac{\left(P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right) \text{Cd}(\text{CH}_3)_2}{\left(P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right) \text{Cd}_{13}} \quad (7)$$

Using the values calculated for P in our CNDO calculation, we obtain the ratio 6.65, which compares well with the experimental (vide supra) ratio of 7.57. Our ratio for $B_2^0(\text{Cd}(\text{CH}_3)_2)/B_2^0(\text{Cd}_{13})$ is 1.95, in poor agreement. In our view this indicates that the substitution of $q_A^e/q_B^e = q_A^n/q_B^n$ in Equation (5) by Bancroft et al.⁸ is unsuitable for comparing cadmium dimethyl with cadmium metal. This result is not surprising. Equation (5) has no theoretical justification, and is not expected to hold for two substances as different as cadmium metal and cadmium dimethyl.

III. Conclusions

The discussion above throws serious doubt on the validity of equating the ratio of a B_2^0 crystal-field parameter for two compounds with the ratio of their nuclear electric field gradients. The calculations imply, without conclusively proving, that a crystal-field model is suitable for the explanation of the enhanced apparent spin-orbit splitting observed by photoemission in the 4d region of cadmium metal.

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