

## A specific heat study on the phase transitions in $\text{Cs}_2\text{ZnI}_4$ below room temperature

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 7481

(<http://iopscience.iop.org/0953-8984/7/38/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:09

Please note that [terms and conditions apply](#).

## A specific heat study on the phase transitions in Cs<sub>2</sub>ZnI<sub>4</sub> below room temperature

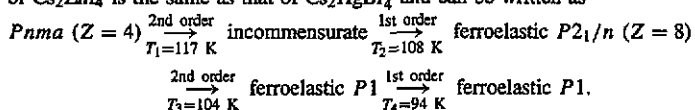
J Díaz-Hernández†, M J Tello†, J M Igartua‡, I Ruiz-Larrea‡,  
T Breczewski‡ and A López-Echarri†

† Departamento de Física de la Materia Condensada, Facultad de Ciencias, UPV/EHU, Apartado 644, Bilbao, 48080, Spain

‡ Departamento de Física Aplicada II, Facultad de Ciencias, UPV/EHU, Apartado 644, Bilbao, 48080, Spain

Received 22 February 1995, in final form 17 May 1995

**Abstract.** Calorimetric measurements of Cs<sub>2</sub>ZnI<sub>4</sub> showed four distinct phase transitions at 117, 108, 104 and 94 K. The shape of the observed specific heat peaks indicates that those at 108 and 94 K are first order in nature. This sequence is in agreement with previous results using different experimental techniques, and supports the hypothesis that the phase transition sequence of Cs<sub>2</sub>ZnI<sub>4</sub> is the same as that of Cs<sub>2</sub>HgBr<sub>4</sub> and can be written as



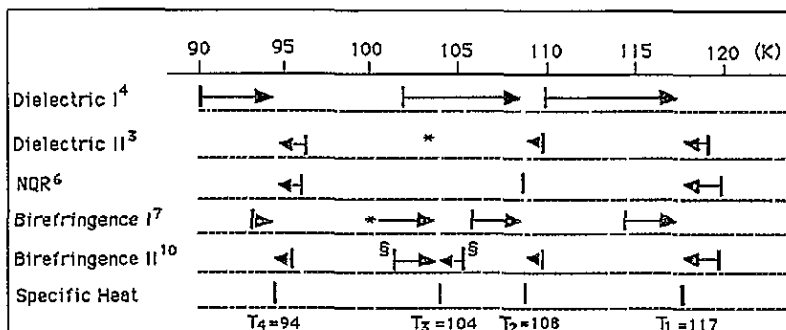
### 1. Introduction

Among the compounds with the A<sub>2</sub>BX<sub>4</sub> general formula some different subfamilies have been proposed in relation to the prototype phase and the number and nature of the phase transition sequences [1]. Most of the compounds studied up to now are members of the K<sub>2</sub>SeO<sub>4</sub> subfamily. In the case of Cs<sub>2</sub>ZnI<sub>4</sub>, which is the subject of this paper, some of the experimental results in the literature define this crystal as analogous to Cs<sub>2</sub>CdBr<sub>4</sub> [1, 2] or to Cs<sub>2</sub>HgBr<sub>4</sub> [1, 3]. In the first case there is a sequence of four phases with three phase transitions which are second, first and second order respectively. In the second case there are five phases with four phase transitions. The phase transitions of this sequence are second, first, second and first order as the temperature is lowered.

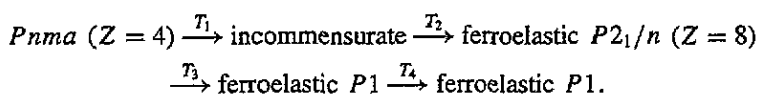
Dielectric [4, 7], NQR [5, 6], NMR [6], thermal expansion [7], birefringence [7] and x-ray [6, 8] measurements as well as optical observations with the polarizing microscope in the Cs<sub>2</sub>ZnI<sub>4</sub> crystal have shown three phase transitions between 120 and 89 K. Dielectric measurements also showed that none of the four phases was ferroelectric. On the basis of the NQR and x-ray data the following sequence of the space groups was proposed: *Pnma* (*Z* = 4) → incommensurate → ferroelastic *P*2<sub>1</sub>/*n* (*Z* = 8) → ferroelastic *P*1 (*Z* = 4). However two facts introduce doubts about this sequence. The first is related to the differences between the transition temperatures obtained by means of different experimental techniques (see table 1). The second is related to the order character of the phase transitions: second order for the *Pnma* → inc, second or first order for the inc → *P*2<sub>1</sub>/*n*, and a clear first order with a noticeable thermal hysteresis for the *P*2<sub>1</sub>/*n* → *P*1 phase transition. These

orders are different to those found for the  $\text{Cs}_2\text{CdBr}_4$  compound. We can conclude that if the proposed sequence is confirmed we would have a new subfamily within the compounds with the  $\text{A}_2\text{BX}_4$  general formula.

**Table 1.** Phase transition sequences. The specific heat data are those found in this paper. The arrows show the correspondence between the phase transition temperatures detected by a set of independent experiments and those obtained by means of adiabatic calorimetry. The (\*) symbol shows those phase transitions not reported in the references but which can be derived from a careful inspection of the published experimental curves (see the text). The § symbol shows the phase transition related to an inflexion point in the birefringence experimental curve. In this case the phase transition temperature could be between 101 K and 106 K.

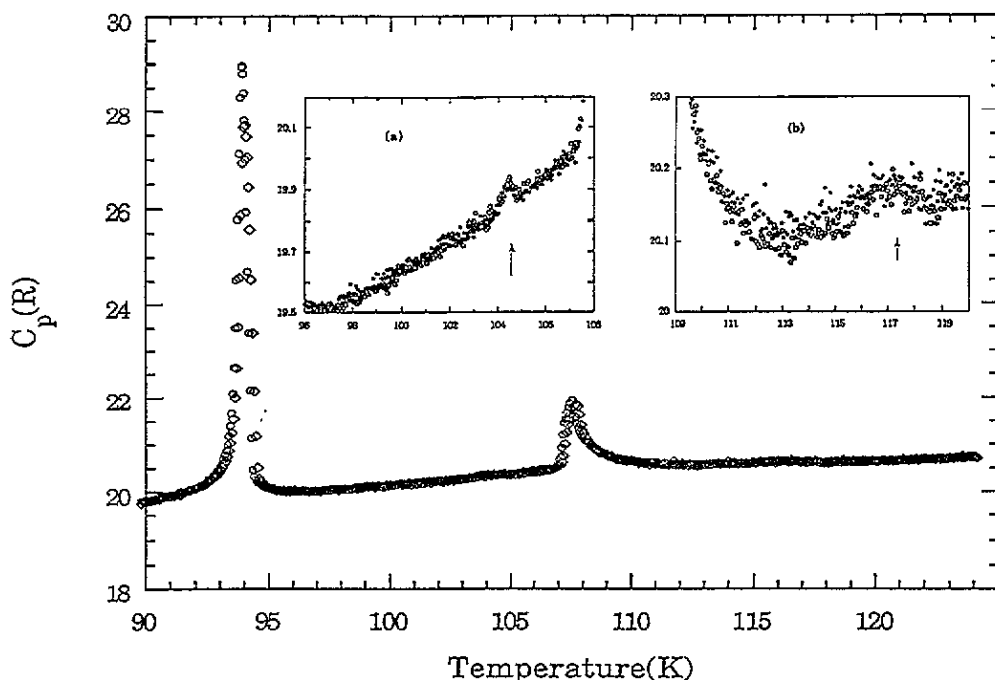


Recent optical and Raman studies [9, 10] suggested a new second-order phase transition between the  $P2_1/n$  and  $P1$  phases with the same triclinic ( $P1$ ) symmetry. In this case the proposed phase transition sequence will be



The transition temperatures of this sequence are shown in table 1. The Raman spectra above and below  $T_4$  indicate either a cell multiplying transition or a symmetry change. These experimental results showed that the number and the orders of the phase transitions (second, first, second and first respectively) are similar to those in the  $\text{Cs}_2\text{HgBr}_4$  crystal [3]. In order to analyse the discrepancies with previous results we must take into account that some experimental techniques are not sensitive enough to detect small anomalies, and also that for the anisotropic quantities we have a different behaviour for each tensor component depending on the symmetry change involved in the phase transition. A preliminary discussion in order to obtain an agreement between the experimental results obtained with the different experimental techniques was given in [10].

However, a complementary measurement of a non-directional physical property with a very highly sensitive experimental technique is necessary in order to confirm whether we have a new subfamily or a new member of the  $\text{Cs}_2\text{HgBr}_4$  subfamily. We have chosen adiabatic calorimetry which was previously used in our laboratory to look for very small anomalies associated with structural phase transitions in crystals with incommensurate phases (see for instance [11]). From the experimental results of this paper we can derive that the  $\text{Cs}_2\text{ZnBr}_4$  crystal shows four phase transitions in agreement with the birefringence data of [9]. In the discussion some remarks derived from the comparison between the experimental results in the literature and our calorimetric measurements are given.



**Figure 1.** The specific heat data for  $\text{Cs}_2\text{ZnI}_4$  obtained from adiabatic calorimetry by the continuous heating technique. Two different thermograms with rates of  $4.3 \text{ K h}^{-1}$  ( $\diamond$ ) and  $1.2 \text{ K h}^{-1}$  ( $\circ$ ) show the specific heat peaks corresponding to the first-order transitions at 94 K and 108 K. Enlargements of the temperature ranges where second-order phase transitions are expected to occur are shown in the insets.

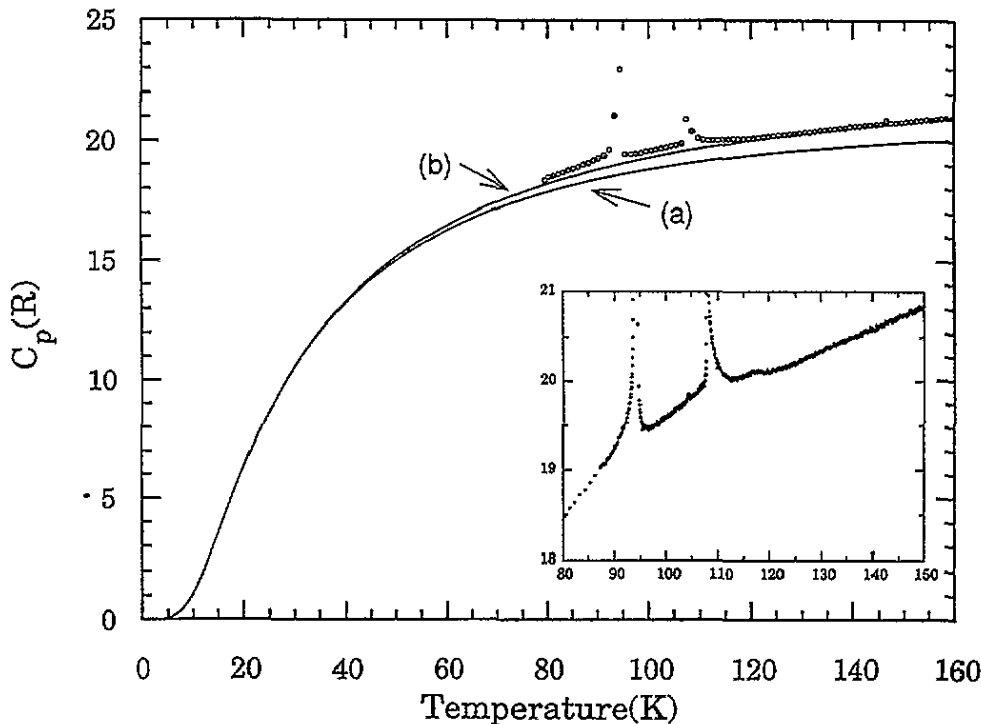
## 2. Experimental details

Small single crystals of  $\text{Cs}_2\text{ZnI}_4$  were obtained from a water solution of  $\text{CsI}$  and  $\text{ZnI}_2$ . The structure and composition were confirmed by chemical analysis and x-ray measurements. A powdered sample was used for the calorimetric measurements. These were done with an automatic adiabatic calorimeter whose characteristics and calibration have been previously described [12–14]. Various heating runs from 80 K to 160 K were performed, using the conventional pulse method with  $1^\circ\text{C}$  temperature steps and also continuous heating thermograms with various heating rates from  $0.4 \text{ K h}^{-1}$  to  $5 \text{ K h}^{-1}$ . This last technique is very sensitive when small specific heat anomalies are present.

## 3. Results and discussion

The experimental results obtained from the discontinuous pulse technique and six different heating thermograms throughout the 80–160 K temperature range clearly showed two calorimetric anomalies associated with the first-order phase transitions at 94 K ( $T_4$ ) and 108 K ( $T_2$ ), in agreement with the results obtained by the discontinuous pulse technique. The expected second-order phase transition at 117 K ( $T_1$ ) was found to have a very low calorimetric signal and required a careful control of the heating procedure. As cited above, another anomaly between the two first-order phase transitions had been suggested by birefringence measurements, probably associated with a new second-order structural phase

transition. In our calorimetric thermograms a repetitive small specific heat peak appeared at 104.5 K ( $T_3$ ) when the heating rates were conveniently reduced. Figure 1 shows the specific heat curves corresponding to the thermograms with  $1.2 \text{ K h}^{-1}$  and  $4.3 \text{ K h}^{-1}$  heating rates. Insets (a) and (b) enlarge the temperature intervals 96–108 K and 109–120 K in order to show the two small  $C_p$  peaks observed in these experiments, which are near to the limits of the experimental resolution.



**Figure 2.** The experimental specific heat of  $\text{Cs}_2\text{ZnL}_4$  obtained by the discontinuous pulse technique together with the theoretical harmonic (a) and harmonic + anharmonic (b) lattice contributions to the specific heat are plotted. The inset shows a thermogram curve with the four phase transitions (heating rate,  $2 \text{ K h}^{-1}$ ).

As in previous works [12], the procedure followed to determine the thermodynamic function values of this phase transition sequence is based on a previous calculation of the baseline associated with the normal lattice specific heat. For this purpose, the harmonic specific heat (which in the following will be identified with the specific heat at constant volume,  $C_v$ ) was constructed from the frequencies of the vibrational lattice modes. In this case, we have fully used the spectroscopic data obtained from Raman experiments [10, 15, 16]. From [10], it seems that the data in [15] and [16] would be better assigned to the  $\text{Cs}_3\text{ZnL}_5$  crystal. However, the discrepancies between the two Raman spectra are not significant for our calculations. In fact, the frequencies of the stretching and bending modes of the  $\text{ZnL}_4$  tetrahedron are practically the same in both works. Some slight but significant differences in the external low-frequency modes are observed, but their contributions to the lattice specific heat attain the saturation values at relatively low temperatures. In table 2 we show the frequency assignments used for our calculations, including their multiplicity. The optical branches were treated by means of single-frequency Einstein functions and the contribution of the acoustic branches was determined using the Debye model for a unique characteristic

frequency  $\nu_D = 35 \text{ cm}^{-1}$ . Although the anharmonic effects are expected to be small in the relatively low-temperature range where the phase transition sequence is present, their contribution to the specific heat should be added to  $C_V$  to obtain the final baseline. As usual we have to resort to the Nernst–Lindemann empirical law [17], which seems to be valid for solids in wide temperature ranges. In the present case we have been able to fit our experimental data with  $a/R \text{ (mol)} = 9.52 \times 10^{-5}$ , where  $a$  is the proportionality constant in the reference above.

**Table 2.** Frequencies and multiplicities used for the determination of the harmonic contribution to the specific heat of  $Cs_2ZnI_4$ . They were obtained from the works by Lamba *et al* [15, 16] (see the text). Only the frequencies at room temperature were used to obtain this contribution. As in previous works [12], the multiplicities (for a molecule) are deduced from the factor group analysis and after taking into account the site symmetry.

	Frequency ( $\text{cm}^{-1}$ )	Multiplicity
Modes in the free molecule treated with Einstein functions		
Internal modes		
$\nu_1(A_1)$	127.0	1
$\nu_2(E)$	60.0	2
$\nu_3(F_1)$	170.0	3
$\nu_4(F_1)$	70.0	3
External modes		
$ZnI_4 = \text{translations}$	35.0	11/4
$ZnI_4 = \text{rotations}$	45.0	3
$2Cs^+$	55.0	21/4
Crystal translations treated with a single Debye function		
$T_x, T_y, T_z$	35.0	1

Figure 2 shows the experimental data obtained by the pulse technique together with the theoretical harmonic and anharmonic contributions to the specific heat. The experimental and theoretical results fit quite well at both sides of the phase transition sequence. Once the baseline values are subtracted, we are able to obtain the local thermodynamic function values for this sequence:  $\Delta H_t = 11.5(RK)$  and  $\Delta S_t = 0.116R$ . At first sight, it seems that the main contribution to the enthalpy and the entropy of the total phase transition sequence arises from the two first-order phase transitions at 94 K and 108 K. However, the proximity of the two peaks makes it difficult to separate the two contributions. Moreover, the calorimetric curve between these two peaks does not fit the baseline established above. A comparison of this behaviour with that of other related compounds with similar phase transition sequences, such as  $Cs_2CdBr_4$  [18], suggests that, in spite of the very low value observed in this case for  $\Delta C_p$  at the normal–incommensurate phase transition at 117 K, a noticeable specific heat tail below this last temperature could also be present. This would lead to a higher enthalpy value for this phase transition. In this situation, only a preliminary assignment of enthalpy and entropy values for the various phase transitions is allowed. In the case of the two first-order phase transitions at 108 K and 94 K, together with the second-order one at 104.5 K, these assignments were obtained from a numerical integration of the specific heat excess, using interpolated straight lines on both sides of the peaks as approximate baselines. Hence, the enthalpy and entropy values for the normal–incommensurate phase at 117 K were obtained by subtraction of these values from  $\Delta H_t$  and  $\Delta S_t$ . The final results are shown in table 3.

**Table 3.** The temperature, enthalpy and entropy associated with the four detected phase transitions in  $\text{Cs}_2\text{ZnI}_4$ .

	Temperature (K)	$\Delta H/(RK)$	$\Delta S/R$
$T_1$	117.17	$3.0 \pm 1$	$0.03 \pm 0.01$
$T_2$	108.07	$2.1 \pm 0.2$	$0.02 \pm 0.002$
$T_3$	104.44	$0.013 \pm 0.004$	$0.00013 \pm 0.00004$
$T_4$	94.16	$6.4 \pm 0.5$	$0.068 \pm 0.005$
Total sequence		11.51	0.118

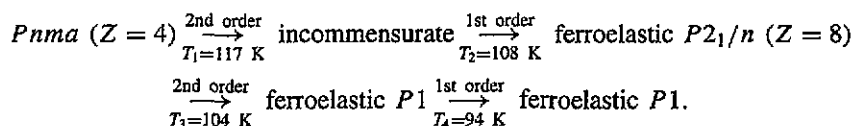
The phase transition sequence established from the calorimetric measurements are consistent with previous birefringence [9] results except in the assignment of temperatures (birefringence II sequence in table 1). However we must say that the adiabatic calorimetry allows a great accuracy in temperature assignment for two reasons: the measurement technique is practically static and the Pt thermometer is in contact with the powdered sample through a helium atmosphere. In the following every time we write a transition temperature reported in the literature we also quote in brackets the equivalent transition temperature determined from adiabatic calorimetry.

Table 1 shows noticeable discrepancies between the transition temperatures obtained by means of two different dielectric measurements. In order to fit these experimental data, it was assumed in [10] that the phase transition at 117 K is not detected in the dielectric I sequence in table 1. However, if we observe that the  $\varepsilon-T$  curves along the  $b$  axis in figures 1 and 5 of [4] and [7] have the same shape, we can conclude that the transition temperatures in the dielectric I sequence in table 1 correspond to the 117 K, 108 K and 94 K transition temperatures of the calorimetric measurements. This means that the temperature axis in [4] is shifted by 5 or 6 K. It is interesting to note here that a careful inspection of the other  $\varepsilon-T$  curves in [4] and [7] allows us to obtain new results. The  $\varepsilon_c-T$  curve in figure 5 of [7] has a small slope change at 104(104) K. At this temperature the specific heat shows a small peak, and the birefringence a small inflection [9]. The observation of the  $\varepsilon_a-T$  curve in [4] allows us to assign a first-order character to the phase transitions at 90(94) K and 102(108) K in agreement with our experimental results. Finally in the  $\varepsilon_a-T$  curve of the same reference there is a clear step at 90(94) K and a very small change at 98(104) K. We can conclude that in the dielectric results of [4] and [7] the phase transition sequence proposed in this paper is present, but the complete sequence is only observed in some crystallographic directions.

A similar discussion can be carried out in the case of birefringence I and II measurements (table 1). Thus, the  $\delta\Delta n_1-T$  curve in figure 2 of [7] shows a very small inflection at 100(104) K, but no anomaly was observed along the other crystallographic directions in the same temperature region. This means that this effect is very small and only detectable in a particular crystallographic direction. The same figure shows that in the (001) crystallographic direction the birefringence is characterized by a jump (first order) at 106(108) K and 93(94) K, but no appreciable change is observed at 104 K. In conclusion we can say that the birefringence results in [7] are in agreement with the birefringence measurements in [9] and therefore with our calorimetric results. In the case of other experimental techniques the results in table 1 are in agreement with the detected phase transitions at 117, 108 and 94 K respectively.

Finally, it is important to remark that in spite of the differences in the transition temperatures between our measurements and other results that appear in the literature it

was possible to clarify, in agreement with [10], that  $Cs_2ZnI_4$  is analogous to  $Cs_2HgBr_4$  and therefore shows the same phase transition sequence:



The temperature discrepancies are in most cases related to the dynamic character of the measurement, the heating or cooling sequence, the local heating of the sample (laser) or the thermal contacts which can produce thermal gradients in the sample. These discrepancies are commonly found even with only one experimental technique such as DSC. In this case noticeable differences (up to 4–5 °C) in the peak temperatures are found when the heating or cooling rates change by 1 °C min<sup>-1</sup>. These differences, which are usually higher in first-order phase transitions due to the thermal hysteresis effects, support our reassignment (table 1) of the transition temperatures found in the literature. In relation to the number of phase transitions observed by means of each experimental technique, it is necessary, as was mentioned before, to know what tensor components are relevant in each step of the phase transition sequence and to have a better experimental accuracy than in [4–7]. In any case the definitive test must be a complete x-ray or neutron diffraction study which will also allow a complete theoretical group analysis.

### Acknowledgments

This work has been sponsored by the Universidad del País Vasco and DGICYT (PB91-0554) Spain. One of the authors (J Díaz-Hernández) gratefully acknowledges Universidad Autónoma de Puebla (Mexico) and also financial support from CONACYT-México.

### References

- [1] Cummins H Z 1990 *Phys. Rep.* **185** 211
- [2] Plesko S, Kind R and Arend M 1980 *Ferroelectrics* **26** 703
- [3] Plesko S, Dvorak V, Kind R and Treindl A 1981 *Ferroelectrics* **36** 331
- [4] Gesi K 1981 *J. Phys. Soc. Japan* **50** 3535
- [5] Aleksandrova I P, Primak S V, Shemetov E V and Kruglik A I 1991 *Sov. Phys.—Solid State* **33** 758
- [6] Aleksandrova I P, Primak S V, Shemetov E V, Kruglik A I and Elizaryev Y G 1990 *Ferroelectrics* **105** 177
- [7] Melinkova S V and Primak S V 1991 *Phase Transitions* **36** 191
- [8] Scaife D E 1971 *Aust. J. Chem.* **24** 1315
- [9] Billesbach D P and Ullman F G 1992 *Phys. Rev. B* **46** 5073
- [10] Billesbach D P and Ullman F G 1993 *Ferroelectrics* **143** 27
- [11] Zubillaga J, López-Echarri A and Tello M J 1988 *J. Phys. C: Solid State Phys.* **21** 4417
- [12] Igartua J M, Ruiz-Larrea I, Couzi M, López-Echarri A and Breczewski T 1991 *Phys. Status Solidi b* **168** 67
- [13] López-Echarri A and Tello M J 1981 *J. Phys. D: Appl. Phys.* **14** 71
- [14] Zubillaga J, López-Echarri A and Tello M J 1985 *Thermochim. Acta* **92** 283
- [15] Lamba O P, Patel M B, Ram S, Chand P and Bist H D 1984 *Solid State Commun.* **50** 321
- [16] Lamba O P and Sinha S K 1986 *Solid State Commun.* **57** 365
- [17] Gopal E S R 1966 *Specific Heat at Low Temperatures* (London: Heywood)
- [18] Igartua J M *et al* to be published