Crystal structure of the ternary semiconductor $Cu_2In_{14/3}\square_{4/3}Se_8$ determined by X-ray powder diffraction data

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(Received 20 December 2016; accepted 17 May 2018)

The crystal structure of the partially ordered vacancy compound $Cu_2In_{14/3}\square_{4/3}Se_8$, belonging to the system I_3-III_7-$\square_2$-VI_{12}, was analyzed using X-ray powder diffraction data. Several structural models were derived from the structure of the selenium-rich phase β-$Cu_{0.39}In_{1.2}Se_2$ by permuting the cations in the available Wyckoff positions. The refinement of the best model by the Rietveld method in the tetragonal space group $P\overline{4}$ 2*c* (No 112), with unit-cell parameters $a = 5.7487(3)$ Å, $c = 11.5106(6)$ Å, $V = 380.40(3)$ Å^3, led to $R_p = 9.0\%$, $R_{wp} = 9.9\%$, $R_{exp} = 7.2\%$, $S = 1.4$ for 134 independent reflections. This model has the following Wyckoff site atomic distribution: Cu in 2*e* (0,0,0); In in 2*b* (½,0,¼), 2*d* (0,½,¼), and 2*f* (½,½,0);□ in 2*f* (½,½,0); Se in 8*n* (*x*,*y*,*z*). © *2018 International Centre for Diffraction Data*. [doi:10.1017/S0885715618000519]

Key words: X-ray powder diffraction, semiconductor, ordered vacancy compound, chemical synthesis, crystal structure

I. INTRODUCTION

The compounds with ternary structures of the chalcopyrite family I-III-VI_2 form an extensive group of semiconductor materials with diverse optical and electrical properties (Shay and Wernik, 1974). From the structural point of view, they crystallize with tetragonal symmetry in the space group $I\overline{4}$ 2*d* (No 122) being isostructural with the $CuFeS_2$ mineral (chalcopyrite) from which they take their name (Pauling and Brockway, 1932). This family of compounds fulfills the rules of formation of adamantane compounds and belongs to the normal semiconductor compound families (Parthé, 1995). In particular, the ternary chalcopyrite semiconductor $CuInSe_2$ has emerged as a leading material for the preparation of photovoltaic devices because of their potential applications in solar cell technology (Rincón *et al*., 2001, 2003).

In recent years, considerable attention has been focused on the detailed study of the ordered vacancy compounds (OVCs) related to the chalcopyrite compounds of the I-III-VI family, particularly $CuInSe_2$ (CIS) (Feaeheiley, 1986; Höenle *et al*., 1988; Knight, 1992; Negami *et al*., 1994; Zhang *et al*., 1997, 1998; Merino *et al*., 2000; Gulay *et al*., 2004; Paszkowicz *et al*., 2004; Wasim *et al*., 2004; among others).

In an interesting paper review, Feaeheiley (1986) studied the phase diagrams of the pseudobinary Cu_2Se-In_2Se_3 system and reports the formation of ternary phases $CuInSe_2$, $Cu_2In_4Se_7$, $CuIn_3Se_5$, $Cu_3In_5Se_9$, Cu_5InSe_4, and $CuIn_5Se_8$. Moreover, several In-rich phases of the $CuInSe_2$ compound are reported to form on the tie-line of the $(Cu_2Se)_X$-$(In_2Se_3)_{1-X}$ pseudo binary system (Zhang *et al*., 1998). In studying the defect physics of $CuInSe_2$, Zhang *et al*. (1998) have suggested that the presence of the donor–acceptor defect pair ($2V^{1-}Cu + In^{2+}Cu$) could be used to explain the existence, according to $Cu_{n-3}In_{n+1}Se_{2n}$, of $CuIn_5Se_8$ ($n = 4$), $Cu_2In_6Se_{10}$ ($CuIn_3Se_5$) ($n = 5$), $Cu_3In_7Se_{12}$ ($n = 6$), $Cu_2In_4Se_7$ ($n = 7$), $Cu_5In_9Se_{16}$ ($n = 8$), $Cu_3In_5Se_9$ ($n = 9$) OVCs because of the repeat of a single unit of this defect pair for each $n = 4$, 5, 6, 7, 8, and 9 units, respectively, of $CuInSe_2$. In addition, Gulay *et al*. (2004) proposed three new phases for this system: $CuIn_7Se_{11}$, $CuIn_{11}Se_{17}$, and $Cu_7In_{13}Se_{23}$.

From the structural point of view, several authors have reported that most of these OVC materials crystallize in chalcopyrite-related structures (Höenle *et al*., 1988; Schmid *et al*., 1993; Negami *et al*., 1994; Marín *et al*., 1998; Merino *et al*., 2000).

In particular, the ternary compound $Cu_3In_7Se_{12}$ ($n = 6$), or more precisely $Cu_3In_7\square_2Se_{12}$, where □ denotes the cation vacancy which is included to maintain the same number of cations and anions sites, belongs to the family of OVCs I_3-III_7-$\square_2$-VI_{12}. For this ternary compound, to the best of our knowledge, there are no data on its crystal structure based on single-crystal or powder X-ray diffraction measurements.

However, a search performed with the Powder Diffraction File (ICDD, 2017) possibly found 15 entries with Cu-In-Se compounds, different compositions, and space group $P\overline{4}$ 2*c*. Among these are the phases $CuIn_3Se_5$ (PDF 51–1221) (Marín *et al*., 1998), $Cu_{0.39}In_{1.2}Se_2$ (PDF 42–862) and $Cu_{0.72}In_{2.16}Se_{3.6}$ (PDF 10–954) (Höenle *et al*., 1988), and $Cu_{0.8}In_{2.4}Se_4$ (PDF 16–4111) (Merino *et al*., 2003).

The chemical formula of the ternary compound reported in this paper can be written as $Cu_3In_7\square_2Se_{12}$ if we take the

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https://doi.org/10.1017/S0885715618000519 Published online by Cambridge University Press

TABLE I. Powder X-ray diffraction data of the ternary $Cu_2In_{14/3}\square_{4/3}Se_8$.

Space group: $P\bar{4}\ 2c$, $a = 5.7505(2)$ Å, $c = 11.450(3)$ Å								
$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
15.402	5.7480	2.0	1	0	0	15.395	5.7505	−0.007
17.248	5.1367	4.9	1	0	1	17.241	5.1388	−0.007
			1	1	0	21.839	4.0662	
21.897	4.0555	2.8	1	0	2	21.888	4.0571	−0.009
26.870	3.3152	100.0	1	1	2	26.870	3.3151	0.000
28.031	3.1804	4.2	1	0	3	28.035	3.1800	0.004
			2	1	0	34.857	2.5717	
34.894	2.5690	3.1	2	0	2	34.889	2.5694	−0.005
			1	0	4	34.985	2.5625	
35.757	2.5090	4.4	2	1	1	35.754	2.5092	−0.003
38.337	2.3458	2.8	2	1	2	38.337	2.3459	0.000
42.337	2.1330	3.5	2	1	3	42.343	2.1327	0.006
44.534	2.0327	39.3	2	2	0	44.526	2.0331	−0.008
			3	0	0	47.386	1.9168	
47.411	1.9159	2.1	2	2	2	47.411	1.9159	0.000
			2	1	4	47.486	1.9130	
48.100	1.8900	2.5	3	0	1	48.087	1.8905	−0.013
52.783	1.7328	27.3	3	1	2	52.774	1.7331	−0.009
63.119	1.4717	2.2	3	2	3	63.124	1.4716	0.005
64.792	1.4377	5.1	4	0	0	64.794	1.4376	0.002
71.459	1.3190	10.1	3	3	2	71.464	1.3189	0.005
72.025	1.3100	3.0	4	1	3	72.029	1.3100	0.004
82.108	1.1728	7.2	4	2	4	82.095	1.1729	−0.013
88.226	1.1066	4.8	5	1	2	88.233	1.1065	0.007
98.520	1.0166	2.8	4	4	0	98.526	1.0165	0.006

Z value ⅔ non-integer with the space group $P\bar{4}\ 2c$ (No 112) or taken the Z value integer equal to 1 in the chemical formula $Cu_2In_{14/3}\square_{4/3}Se_8$ with the same space group. Therefore, in this work, a detailed structural analysis of the new ternary compound $Cu_2In_{14/3}\square_{4/3}Se_8$ was performed using X-ray powder diffraction, aiming to derive a model that explains all the diffraction peaks in the powder pattern, and to refine it by means of the Rietveld method. The chemical structure was validated using the bond valence sum (BVS) calculations (Brown and Altermatt, 1985; Brese and O'Keeffe, 1991).

II. EXPERIMENTAL

A. Synthesis

The first step is to prepare the synthesis of the compound, the required masses of Cu, In, and Se of 6*N* of purity were sealed under vacuum in a quartz ampoule, then heated slowly (5 °C h^{-1}) up to 1000 °C and left at that temperature for 48 h. It was slowly cooled down (10 °C h^{-1}) to approximately 650 °C and then annealed, at this temperature, 100 h before cooling to room temperature. The resulting ingots were used to grow the single crystal by chemical vapor deposition (CVD) with small amount (5 mg cc^{-1}) of the volatile element, such as iodine, to form volatile compounds of the synthesis element to promote transport and vapor phase mixing for subsequent condensation of single crystal of the compound. This CVD is carried out in a two-zone furnace. The crushed powder of the compound and the I_2 was placed in the hotter zone (600 °C), and the crystal was grown in the lower furnace (550 °C).

B. Powder diffraction data collection

For the X-ray analysis, a small quantity of the sample, cut from the ingot, was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at 293(1) K, in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (Cu$K\alpha$1 radiation: $\lambda = 1.54056$ Å; 40 kV; 30 mA). A fixed aperture and divergence slit of 1 mm, a 1 mm monochromator slit, and a 0.1 mm detector slit were used. The specimen was scanned from 10° to 100° 2θ, with a step size of 0.02° and a counting time of 10 s. Quartz was used as an external standard. The Bruker AXS analytical software was used to establish the positions of the peaks. Further crystallographic details, including atomic coordinates, are included in the supplementary material.

III. RESULTS AND DISCUSSION

The X-ray diffractogram of $Cu_2In_{14/3}\square_{4/3}Se_8$ shows a single phase. The 2θ positions of the 20 first peaks in the diffraction pattern were introduced into the auto-indexing program Dicvol04 (Boultif and Louër, 2004), and a tetragonal cell of dimensions $a = 5.746(1)$ Å, $c = 11.515(1)$ Å, were obtained. This cell is similar in magnitude to the parent chalcopyrite structure of $CuInSe_2$, $a = 5.781(1)$ Å, $c = 11.642(3)$ Å (Knight, 1992). The lack of systematic absence condition $h + k + l$ in the general reflections of the type hkl indicating a P-type cell and rule out the I-type cell of the chalcopyrite structure. In addition, the conditions hhl: $l = 2n$ and $00l$: $l = 2n$ suggest the extension symbol $P\bar{4}\ 2c$.

The complete powder diffraction dataset was reviewed in the tetragonal space group $P\bar{4}\ 2c$ by using the program NBS*AIDS (Mighell *et al.*, 1981). From this analysis, the refined unit-cell parameters obtained were: $a = 5.7505(2)$ Å and $c = 11.450(3)$ Å, with figures of merit $M_{20} = 65.9$ (de Wolff, 1968) and $F_{20} = 28.6$ (0.0057, 122) (Smith and

TABLE II. Models employed in the Rietveld refinement for $Cu_2In_{14/3}\square_{4/3}Se_8$.

Model	(2*e*)	(2*b*)	(2*d*)	(2*f*)	(8*n*)	R_p	R_{wp}	S
	0,0,0	½,0,¼	0,½,¼	½,½,0	*x*,*y*,*z*			
1	Cu	In1	In2	In3 + □	Se	9.0	9.9	1.4
2	Cu	In1	In3 + □	In2	Se	11.7	17.0	2.4
3	Cu	In2	In1	In3 + □	Se	31.0	47.1	6.5
4	Cu	In2	In3 + □	In1	Se	12.0	18.5	2.6
5	Cu	In3 + □	In1	In2	Se	12.8	18.1	2.5
6	Cu	In3 + □	In2	In1	Se	18.7	25.1	3.5

In3 (cation) (foc = ⅓), □ (vacancy) (foc = ⅔), Se (anion): ($x \approx ¼$, $y \approx ¼$, $z \approx ⅛$).

https://doi.org/10.1017/S0885715618000519 Published online by Cambridge University Press

TABLE III. Rietveld refinement results for $Cu_2In_{14/3}\square_{4/3}Se_8$.

Molecular formula	$Cu_2In_{14/3}\square_{4/3}Se_8Cu_3In_7\square_2Se_{12}$	Wavelength (Cu$K\alpha$)	1.54056 Å
Molecular weight (g mol^{-1})	1294.6	Data range 2θ (°)	10–100
a (Å)	5.7487 (3)	Step size 2θ (°)	0.02
c (Å)	11.5106 (6)	Counting time (s)	40
c/a	2.00	Step intensities	4501
V (Å^3)	380.40 (3)	Independent reflections	134
Z	1	R_p (%)	9.0
Crystal system	Tetragonal	R_{wp} (%)	9.9
Space group	$P\bar{4}$ 2c (No 112)	R_{exp} (%)	7.2
d_{calc} (g cm^{-3})	5.65	R_B (%)	8.1
Temperature (K)	298 (1)	S	1.4

$R_{exp} = 100\ [(N - P + C)/\Sigma_w(y_{obs}^2)]^{1/2}$ $R_p = 100\ \Sigma|y_{obs} - y_{calc}|/\Sigma|y_{obs}|$.
$R_{wp} = 100\ [\Sigma_w|y_{obs} - y_{calc}|^2/\Sigma_w|y_{obs}|^2]^{1/2}$ $S = [R_{wp}/R_{exp}]$.
$R_B = 100\ \Sigma_k|I_k - Ic_k|/\Sigma_k\ |I_k|$ N − P + C is the number of degrees of freedom.

Snyder, 1979). The resulting X-ray powder diffraction data for $Cu_2In_{14/3}\square_{4/3}Se_8$, together with the observed and calculated 2θ, the d-spacing as well as the relative intensities of the reflections, are given in Table I.

A search in the ICSD Database (ICSD, 2008) showed an early report by Höenle *et al.* (1988) of a selenium-rich phase β-$Cu_{0.39}In_{1.2}Se_2$, which was solved by single crystal in the space group $P\bar{4}$ 2c. The similarity in the space group symbol with our structure gave indications that the β-$Cu_{0.39}In_{1.2}Se_2$ structure could be a good starting point to construct the initial structural model for $Cu_2In_{14/3}\square_{4/3}Se_8$. Thus, several models were derived from Höenle's structure by permuting the cations in the available Wyckoff positions. Table II shows six models tested against the diffraction data by means of the Rietveld refinement method (Rietveld, 1969), all of which have the Cu cation placed in the origin with Wyckoff position (2e): 0,0,0. Other tests were performed where the Cu cation was moved from the (2e) position or In cations placed in the (2a) or 2(c) position, and only poor quality Rietveld refinement fits were obtained, and therefore, not presented here.

The Rietveld refinements were carried out using the Fullprof program (Rodriguez-Carvajal, 1993, 2016). The angular dependence of the peak full width at half maximum was described by the Cagliotti's formula (Cagliotti *et al.*, 1958). Peak shapes were described by the parameterized Thompson–Cox–Hastings pseudo-Voigt profile function (Thompson *et al.*, 1987). The background variation was described by a polynomial with six coefficients. The thermal motion of the atoms was described by one overall isotropic temperature factor. From the figures of merit R_p, R_{wp}, and S, it was inferred that the model that best fits the diffraction data is model 1, from Table II. The results of the Rietveld refinement for model 1 are summarized in Table III. Figure 1 shows the observed, calculated, and difference profile for the final cycle of Rietveld refinement. Atomic coordinates, isotropic temperature factor, bond distances, and angles are reported in Table IV.

$Cu_2In_{14/3}\square_{4/3}Se_8$ is a partial OVC (Zhang *et al.*, 1997), which crystalize in a P-chalcopyrite structure (Höenle *et al.*, 1988), and consists of a three-dimensional arrangement of distorted $CuSe_4$ and $InSe_4$ tetrahedral connected by common faces. In this structure, each Se atom is coordinated by four cations (one Cu and three In) located at the corners of a slightly distorted tetrahedron. In the same way, each cation

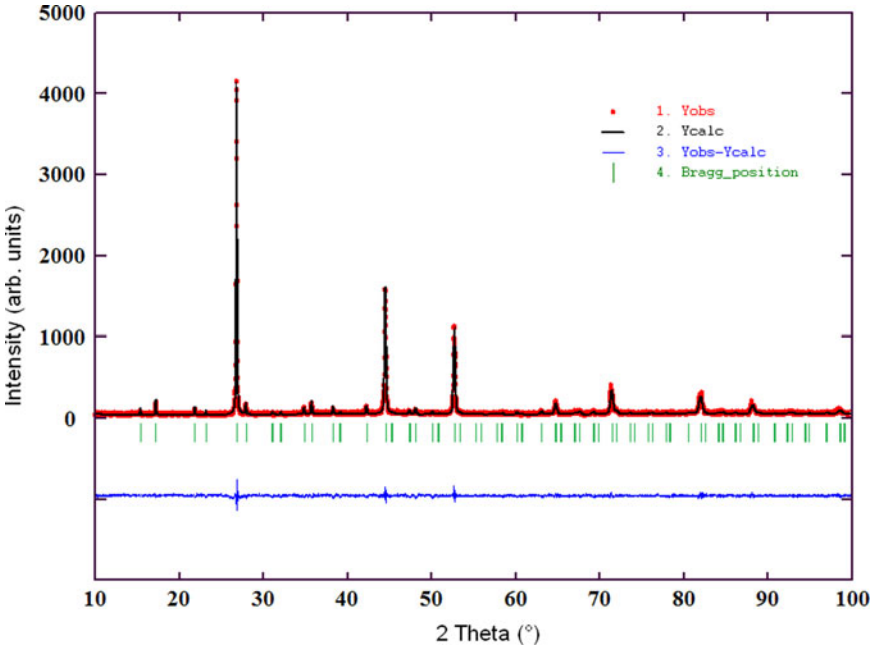


Figure 1. (Color online) Final Rietveld refinement plot for $Cu_2In_{14/3}\square_{4/3}Se_8$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

https://doi.org/10.1017/S0885715618000519 Published online by Cambridge University Press

TABLE IV. Atomic coordinates, isotropic temperature factors, and bond distances (Å) for $Cu_2In_{14/3}\square_{4/3}Se_8$, derived from the Rietveld refinement. Bond valence sum (BVS) are also showed.

Atom	Ox.	BVS	Site	*x*	*Y*	*z*	foc	*B* (Å^2)
Cu	+1	1.3	2*e*	0	0	0	1	0.5 (5)
In1			2*b*	½	0	¼	1	0.5 (5)
In2	+3	3.3	2*d*	0	½	¼	1	0.5 (5)
In3 + □			2*f*	½	½	0	In3(⅓) + □(⅔)	0.5 (5)
Se	−2	2.4	8*n*	0.217 (1)	0.267 (1)	0.121 (1)	1	0.5 (5)
Cu–Se^{i}	2.419 (8)	In1–Se^{iii}	2.685(8)	In2–Se^{ii}	2.357 (9)	In3–Se^{iv}	2.526 (8)	

Symmetry codes: $^{(i)}$ *y*, −*x*, −*z*; $^{(ii)}$ 1−*x*, 1−*y*, *z*; $^{(iii)}$ *x*, −*y*, 0.5−*z*; $^{(iv)}$ −*x*, *y*, 0.5−*z*.
(BVS): $V_i = \sum_j \exp[(R_o - R_{ij})/b]$, $b = 0.37$ Å, R_o (Cu–Se) = 2.02 Å, R_o (In–Se) = 2.47 Å.

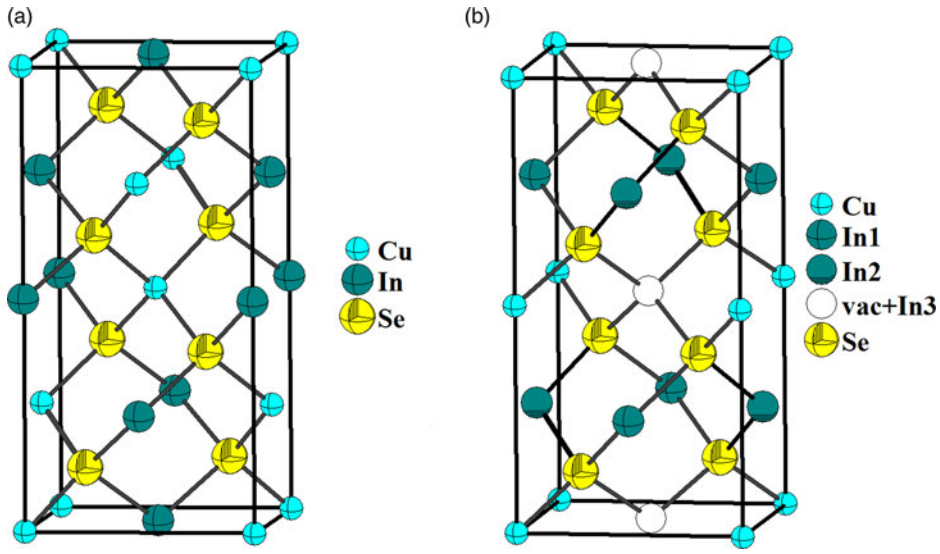


Figure 2. (Color online) Unit-cell diagram for the chalcopyrite (a) $CuInSe_2$ compared with the new (b) *P*-chalcopyrite $Cu_2In_{14/3}\square_{4/3}Se_8$.

is tetrahedrally bonded to four anions. This array is expected for adamantane compounds (Parthé, 1995). Figure 2 shows the unit-cell diagram for $Cu_2In_{14/3}\square_{4/3}Se_8$ compound compared with the chalcopyrite $CuInSe_2$ parent, where it is possible to observe the different In cation sites and vacancy sites. In *P*-chalcopyrite structure, the introduction of the additional In cations produces its "dilution" in the chalcopyrite structure, which leaves the cell volume unchanged.

The Cu–Se [2.419(8) Å] and In–Se [2.523(8) Å average] bond distances compare well with those observed in other adamantine structure compounds such as $CuInSe_2$ (2.432–2.591 Å) (Knight, 1992), $Cu_2FeSnSe_4$ (2.417 Å) (Roque-Infante *et al*., 1997), Cu_2SnSe_3 (2.415 Å average) (Delgado *et al*., 2003), $CuFe_2(Al,Ga,In)Se_4$ (2.417–2.50 Å average) (Delgado *et al*., 2008, 2015), $CuFe(Al,Ga,In)Se_3$ (2.421–2.520 Å average) (Mora *et al*., 2007; Delgado *et al*., 2009), $CuNi(Ga,In)Se_3$ (2.420–2.500 Å average) (Delgado *et al*., 2010), Cu_2GeSe_4 (2.42 Å) (Choi *et al*., 2013), $CuZn(Al,Ga,In)Se_3$ (2.427–2.530 Å average) (Delgado *et al*., 2016), $CuMn_2InSe_4$ (2.447–2.594 Å) (Delgado and Sagredo, 2016).

The chemical structural model was checked by the analysis of the interatomic distances using the BVS formula based on bond-strength examination (Brown and Altermatt, 1985; Brese and O'Keeffe, 1991). The commonly adopted expression for the BVS is $v_{ij} = \exp[(R_o - d_{ij})/B$, where d_{ij} is the interatomic distance and *B* is a "universal" constant equal to 0.37 Å. The values for the reference distance R_o for Cu–Se and In–Se are 2.02 and 2.47 Å, respectively. Table IV also shows the BVS results for $Cu_2In_{14/3}\square_{4/3}Se_8$, indicating that the oxidation state for each ion is in good agreement with the expected formal oxidation state of Cu^+, In^{3+}, and Se^{2-} ions.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715618000519.

ACKNOWLEDGEMENTS

This work was supported by FONACIT (Fondo Nacional de Investigaciones Científicas, grant LAB-97000821).

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https://doi.org/10.1017/S0885715618000519 Published online by Cambridge University Press