

# SUPPLEMENTARY MATERIAL: The infrared vibrational spectrum of andradite-grossular solid solutions. A quantum-mechanical simulation

M. De La Pierre,<sup>1</sup> Y. Noël,<sup>2</sup> S. Mustapha,<sup>3</sup> A. Meyer,<sup>1</sup> Ph. D'Arco,<sup>2</sup> and R. Dovesi<sup>1</sup>

<sup>1</sup>*Dipartimento di Chimica, Università di Torino and NIS -  
Nanostructured Interfaces and Surfaces - Centre of Excellence,  
<http://www.nis.unito.it>, Via P. Giuria 7, 10125 Torino, Italy*

<sup>2</sup>*Institut des Sciences de la Terre de Paris (UMR 7193 UPMC-CNRS),  
UPMC, Sorbonne Universités, Paris, France*

<sup>3</sup>*Centre de Mathématiques de Jussieu (UMR 7193 UPMC-CNRS),  
UPMC, Sorbonne Universités, Paris, France*

(Dated: December 3, 2012)

## I. VIBRATIONAL PROPERTIES: CONSTRUCTION OF THE IR BANDS

We here discuss in detail the definition and construction of the IR bands, which has only been outlined in the “Vibrational properties: general features” Section in the Paper. Let us recall that, for convenience, the spectral range was divided in two regions, i.e. below ( $L\nu$ ) and above ( $H\nu$ ) 700  $\text{cm}^{-1}$  (L and H stand for low and high frequency).

We are willing to simplify the discussion by focusing on the dominant features of the infrared spectra. The end members (see Figure 4 in the Paper) show four very intense bands with maxima at 277.8, 363.9, 792.4 and 866.9  $\text{cm}^{-1}$  (Adr), and at 386.3, 432.7, 827.8 and 900.6  $\text{cm}^{-1}$  (Grs). When moving to binary systems, active modes (three-fold degenerate,  $F_{1u}$  symmetry) split, and many others become active. Let us take  $L1$  (Adr),  $L2$  and  $L14$  configurations as an example.

Figure 1 and Table I refer to the high frequency  $H\nu$  region; up to 15 and 8 modes appear for  $L14$ , in the frequency ranges of the 792.4 and 866.9  $\text{cm}^{-1}$  bands of Adr, respectively (the end member shows only 2 and 1 modes). We notice that the convolution of such large sets of modes in the binaries nearly coincides with the two bands of the end members.

The case of the low frequency  $L\nu$  region is given in Figure 2 and Table I. For lowly substituted binaries (1-2 atoms, e.g.  $L2$ ) the convolution of the IR active modes still results in two well-defined spectral features (although differing in shape from the end members ones). In highly substituted binaries (3-5 atoms, e.g.  $L14$ ) the 290 ( $x_{Al}=3$ ) - 380 ( $x_{Al}=5$ )  $\text{cm}^{-1}$  range shows a large number of modes of similar intensity (24 in the case of  $L14$ ), which makes the identification of bands more difficult and the correspondence with the end members looser, whereas a well-defined feature is

still found in the 370 ( $x_{Al}=3$ ) - 440 ( $x_{Al}=5$ )  $\text{cm}^{-1}$  range (including up to 13 modes in L14). In the following, we will call IR bands the four sets of features along the solid solution series described above, which mimic the four intense structures in the end members spectra; they are labeled as  $L\nu(1)$ ,  $L\nu(2)$  and  $H\nu(3)$ ,  $H\nu(4)$ , respectively.

Each band is attributed the frequency of its most intense mode (“ $\nu$ ” in Table 2 in the Paper). The integrated intensity (“ $II$ ” in the Table) of the four bands shows a very regular trend along the series from one end member to the other, indicating that  $II$  is a significant quantity for our investigation. For each band,  $II$  is the sum of the intensities of all modes within the corresponding band range. The definition of this range is obvious for  $H\nu(3)$  and  $H\nu(4)$ , as these two bands are well separated in all configurations. For  $L\nu(1)$  and  $L\nu(2)$  bands, we applied a criterium based on isotopic substitution: modes were included in a given band range if showing an isotopic shift  $\Delta\nu_{iso} > 5 \text{ cm}^{-1}$ , upon substitution of an atomic species characterizing that band (“type” in Table 2 in the Paper). Note that, given the high number of modes of similar intensity in highly substituted binaries, this criterium was not applied to the dataset of modes, but rather to the curves of the IR spectra (see Figure 5 in the Paper, which is discussed in detail in the Section “IR wavenumbers” in the Paper). As a consequence, an uncertainty in the order of a few hundreds  $\text{km/mol}$  should be considered for  $II$  values.

## II. IR SPECTRA AT 300 K

We here report the infrared spectra (Figure 3) and the isotopic substitution spectra (Figure 4) constructed by using the Boltzmann occupation probabilities  $\mathcal{P}_L$  at 300 K, listed in Table II.

They can be compared with Figures 4 and 5 in the Paper ( $T = 1300 \text{ K}$ ), to get an idea of the effect of the temperature value chosen for  $\mathcal{P}_L$  on the computed spectra: indeed, the two sets of spectra are extremely similar to each other. In the experiments, samples are synthesized at high temperatures ( $\geq 1300 \text{ K}$ ), and ionic diffusion processes causing cation exchange are likely to be suppressed as temperature goes down. Thus, the high temperature probabilities adopted in the Paper are more realistic than room temperature ones adopted in this Section.

Note that results and discussion proposed in the Paper are not affected by the choice of temperature, as they refer to the full dataset for the 23 configurations, and not on the weight-averaged data based on the probabilities.

## Figures

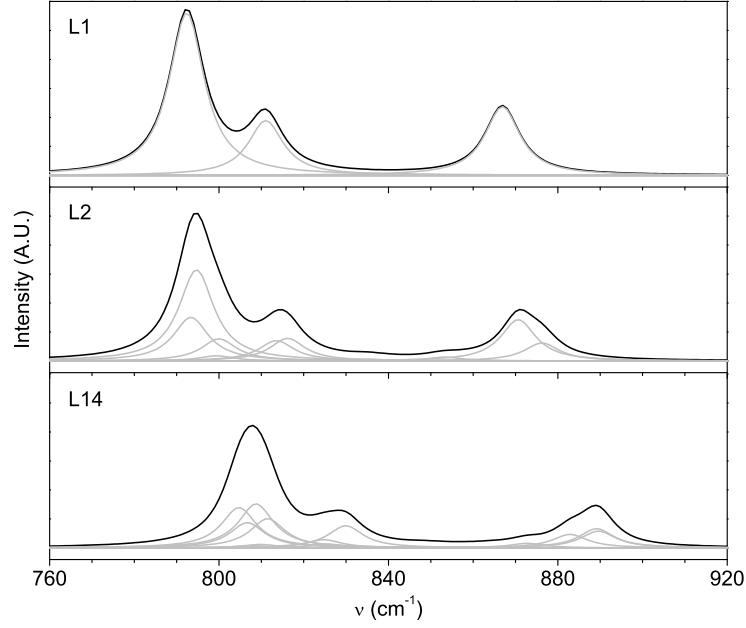


FIG. 1: Convolution of the Lorentzian peaks for the calculated spectra of  $L1$ ,  $L2$  and  $L14$  configurations, with focus on the high frequency ( $H\nu$ ) bands.  $H\nu(3)$  ( $H\nu(4)$ ) band is made up of 2 (1), 10 (5), 15 (8) modes in the three cases, respectively; the corresponding frequencies and intensities are reported in Table I. Even if the number of modes is largely different for the three configurations, it is evident that the corresponding convolutions are very similar. Spectra are constructed as follows: a Lorentzian function is associated to each calculated frequency ( $\nu$ ); the peak area is the calculated intensity; the peak width is set to  $\gamma = 9 \text{ cm}^{-1}$  (see the “Computational details” Section in the Paper).

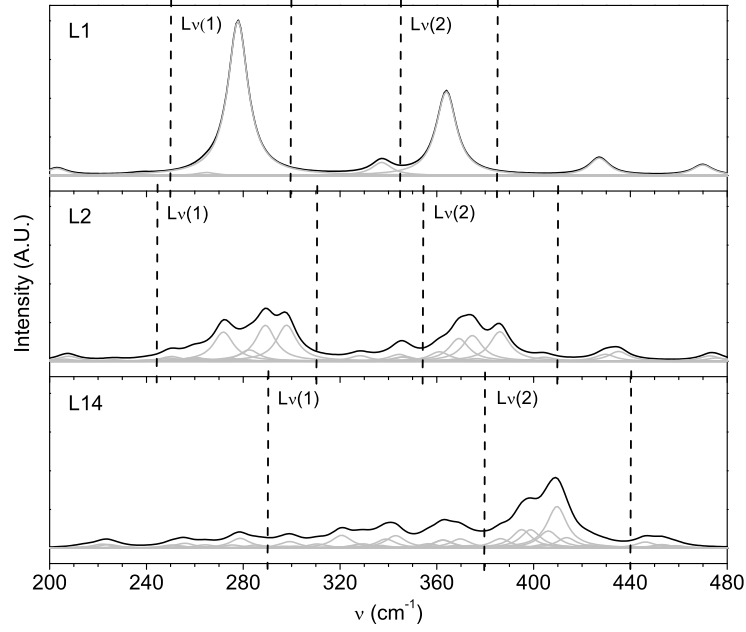


FIG. 2: Convolution of the Lorentzian peaks for the calculated spectra of  $L1$ ,  $L2$  and  $L14$  configurations, with focus on the low frequency ( $L\nu$ ) bands.  $L\nu(1)$  ( $L\nu(2)$ ) band is made up of 2 (1), 13 (8), 24 (13) modes in the three cases, respectively; the corresponding frequencies and intensities are reported in Table I; vertical lines indicate the range of  $L\nu(1)$  and  $L\nu(2)$  bands, used to compute the integrated intensities  $II$  (see the text).  $L14$  is the configuration whose  $L\nu$  bands show the largest number of modes. Spectra are constructed as in Figure 1 in this Supplementary Material.

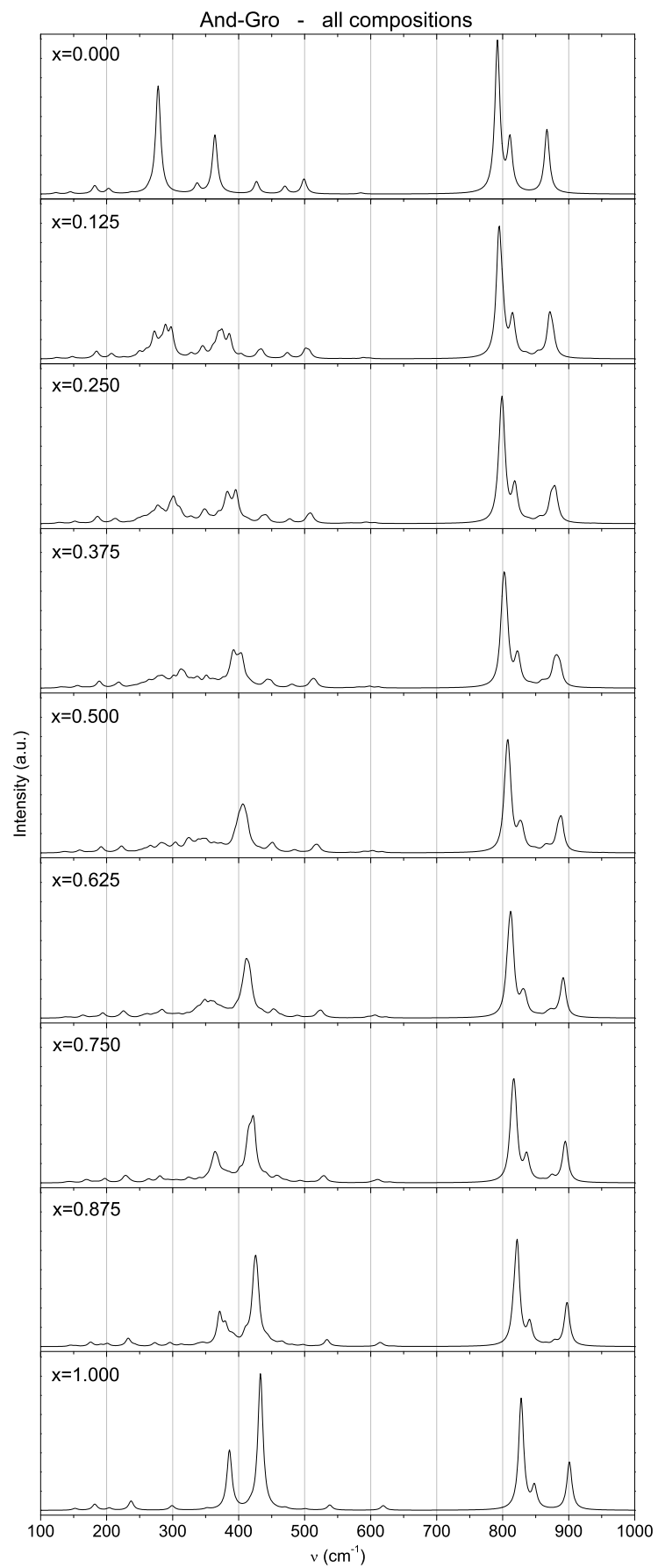


FIG. 3: Calculated infrared spectra at 300 K for nine compositions of the Adr-Grs solid solutions, with  $x$  ranging from 0 (Adr) to 1 (Grs), in steps of 0.125 (number of Al atoms  $n_{Al}=0-8$ ). Spectra are constructed as in Figure 1 in this Supplementary Material. In the case of compositions corresponding to more than one symmetry independent configuration ( $x_{Al}=0.25-0.75$ ), spectra are averaged with  $\mathcal{P}$  (the occupation probability of the  $L^{th}$  configuration at 300 K and optimized cell volume) weights, as described in the “Computational details” Section in the Paper.

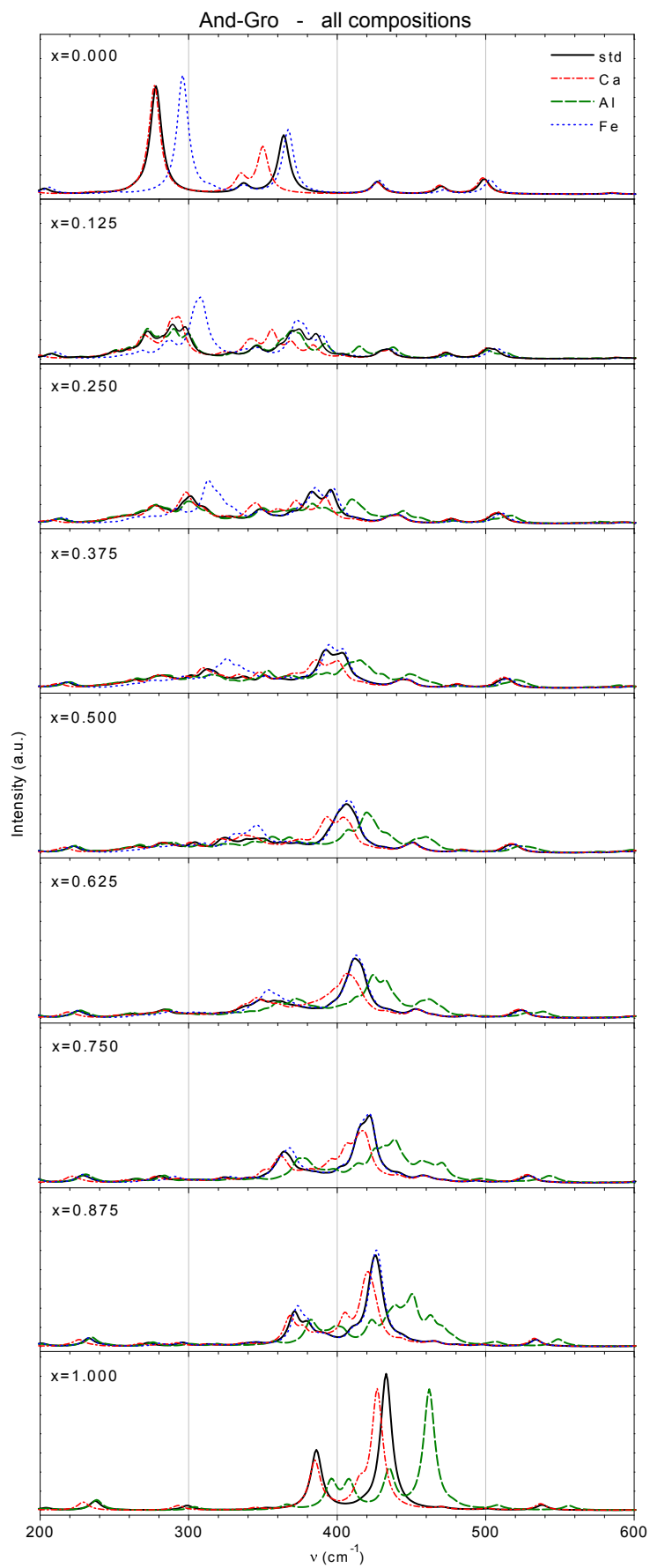




FIG. 4: Effect of cation isotopic substitution on the calculated spectra at 300 K of nine compositions of the Adr-Grs solid solutions, with  $x$  ranging from 0 (Adr) to 1 (Grs), in steps of 0.125 (number of Al atoms  $n_{Al}=0-8$ ). Only the low frequency range  $200-600\text{ cm}^{-1}$  is plotted. Isotopic spectra are obtained by increasing (Ca) or decreasing (Al and Fe) the masses of the corresponding cations by 20%. Spectra are constructed as in Figure 3 in this Supplementary Material.

## Tables

$L$	$L\nu(1)$		$L\nu(2)$	$H\nu(3)$	$H\nu(4)$
1	264.8 ( 310 )		363.9 ( 8542 )	792.4 ( 22042 )	866.9 ( 9323 )
	277.8 ( 15716 )			811.0 ( 7437 )	
	$w=50$ $II=16026$		$w=40$ $II=8542$	$w=80$ $II=29479$	$w=60$ $II=9323$
2	249.3 ( 313 )	289.2 ( 3649 )	361.0 ( 962 )	793.4 ( 5931 )	850.4 ( 8 )
	250.3 ( 476 )	297.9 ( 3670 )	367.6 ( 154 )	794.7 ( 12363 )	853.2 ( 531 )
	258.7 ( 304 )	304.6 ( 13 )	369.1 ( 2313 )	799.4 ( 706 )	859.5 ( 171 )
	260.0 ( 391 )		374.7 ( 2614 )	800.0 ( 3013 )	870.7 ( 5612 )
	264.0 ( 225 )		376.0 ( 259 )	813.6 ( 2774 )	876.2 ( 2450 )
	271.8 ( 2966 )		386.0 ( 3005 )	816.2 ( 3079 )	
	274.3 ( 279 )		403.6 ( 17 )	830.0 ( 1 )	
	276.5 ( 128 )		404.4 ( 409 )	833.4 ( 87 )	
	278.3 ( 203 )			835.6 ( 256 )	
	282.5 ( 1150 )			839.4 ( 55 )	
	$w=65$ $II=13766$		$w=55$ $II=9733$	$w=85$ $II=28264$	$w=65$ $II=8771$
14	293.9 ( 96 )	356.5 ( 253 )	386.4 ( 959 )	804.7 ( 5466 )	860.2 ( 84 )
	296.7 ( 189 )	362.4 ( 812 )	393.8 ( 209 )	806.7 ( 3428 )	864.7 ( 181 )
	299.1 ( 663 )	362.7 ( 815 )	395.1 ( 1873 )	807.8 ( 303 )	869.9 ( 11 )
	301.4 ( 194 )	367.1 ( 230 )	398.8 ( 1864 )	808.7 ( 5985 )	871.0 ( 74 )
	310.6 ( 423 )	368.2 ( 150 )	404.4 ( 373 )	809.7 ( 478 )	872.7 ( 621 )
	317.3 ( 119 )	369.7 ( 938 )	406.1 ( 1743 )	811.5 ( 3964 )	882.9 ( 1844 )
	320.5 ( 24 )	373.7 ( 251 )	409.7 ( 4235 )	824.7 ( 1120 )	889.1 ( 2601 )
	320.7 ( 1296 )	378.0 ( 97 )	412.5 ( 200 )	825.6 ( 515 )	889.6 ( 2282 )
	327.8 ( 362 )	378.8 ( 177 )	413.7 ( 1061 )	829.9 ( 3017 )	
	329.6 ( 430 )		421.9 ( 105 )	836.0 ( 16 )	
	333.0 ( 159 )		423.1 ( 317 )	843.2 ( 3 )	
	336.5 ( 274 )		428.9 ( 206 )	846.2 ( 111 )	
	339.0 ( 916 )		434.7 ( 10 )	848.5 ( 69 )	
	343.0 ( 1268 )			851.5 ( 135 )	
	356.5 ( 440 )			856.2 ( 56 )	
	$w=90$ $II=10577$		$w=60$ $II=13156$	$w=90$ $II=24664$	$w=60$ $II=7699$

TABLE I:  $L1$ ,  $L2$  and  $L14$  configurations: list of frequencies [ $\text{cm}^{-1}$ ] and intensities [ $\text{km/mol}$ ], in brackets, included within the ranges of the four IR bands. For each band of each configuration,  $w$  is the width [ $\text{cm}^{-1}$ ] and  $II$  is the integrated intensity [ $\text{km/mol}$ ]. See the text for a detailed discussion.

$n_{Al}$	$x_{Al}$	$L$	$\mathcal{M}$	$\mathcal{P}$	$E$
0	0.000	1	1	1.00	-25329.009255
1	0.125	2	8	1.00	-24307.909270
2	0.250	3	4	0.03	-23286.809829
		4	12	0.17	-23286.810429
		5	12	0.80	-23286.811932
3	0.375	6	8	0.02	-22265.711008
		7	24	0.16	-22265.712168
		8	24	0.83	-22265.713755
4	0.500	9	2	0.00	-21244.611745
		10	6	0.02	-21244.614554
		11	6	0.45	-21244.617388
		12	8	0.17	-21244.616212
		13	12	0.20	-21244.615942
		14	12	0.10	-21244.615318
		15	24	0.06	-21244.614098
5	0.625	16	8	0.01	-20223.515980
		17	24	0.18	-20223.517663
		18	24	0.81	-20223.519084
6	0.750	19	4	0.05	-19202.421393
		20	12	0.10	-19202.421131
		21	12	0.85	-19202.423139
7	0.875	22	8	1.00	-18181.326902
8	1.000	23	1	1.00	-17160.232209

TABLE II: Boltzmann occupation probabilities  $\mathcal{P}$  at 300 K and total energies  $E$  (in Hartree, referring to the primitive cell with 80 atoms and including the vibrational zero-point energy) for Adr-Grs solid solutions.  $n_{Al}$  and  $x_{Al}$  are the number and the fraction of Al atoms in the Y sites, respectively;  $n_{Al}$  refers to the primitive cell.  $L$  labels the symmetry independent configurations;  $\mathcal{M}$  is the multiplicity of each configuration.