Supporting information

Mn^{2+} doped $CdAl_2O_4$ Phosphors with New Structure and Special Fluorescence Properties: Experimental and Theoretical Analysis

Weiguang Ran,[†] Lili Wang,[†] Qingzhi Liu,[†] Guangzeng Liu,[‡,§] Dan Qu,[†] Xiaohua Pan,[†] Jinsheng Shi*[†]

[†]Qingdao Agricultural University, Qingdao 266109, People's Republic of China.

[‡]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China.

[§]College of Chemistry and Chemical Engineering, Qilu Normal University, Jinan, 250013, PR China.

Details of the Crystal structure refinements

In our study, the Zn_2SiO_4 (ICSD-67235) phase can be defined as the original structural model for the refinement of the $CdAl_2O_4$ and $CdAl_2O_4$:Mn^{2+} sample due to their similar trigonal structure with the space group R-3 (148). The $CdAl_2O_4$ structure model was coming from the Zn_2SiO_4 structural through substituting eighteen Cd^{2+} atoms for Si^{4+}, and substituting thirty-six Al^{3+} atoms for Zn^{2+}. The single-phase of $CdAl_2O_4$ and $CdAl_2O_4$:Mn^{2+} powders were successfully synthesized in this study, crystallized with the space group of R-3 (148). All atom positions, fraction factors, and temperature factors were refined to convergence and satisfied the reflection conditions well. For pure $CdAl_2O_4$ phosphor, the cell parameter is a = b = 14.2210 Å, c= 9.5733 Å, V = 1676.69 $Å^3$. The final refinement converged with weighted profiles of R_p = 6.03%, R_{wp} = 8.41% and χ^2 = 2.624, which illustrates there is no detectable impurity phase observed in this obtained sample.

Details of the calculation

The CASTEP program was employed to perform geometry optimization using the generalized gradient approximation (GGA) by the Perdew-Burke-Ernzerhof (PBE)[1, 2] formulation. In this calculation, the structure models of $CdAl_2O_4$ and $CdAl_2O_4$:Mn^{2+} phosphors were based on the pure $CdAl_2O_4$ host which was optimized by GSAS program. One of the eighteen Cd atomics was substituted by Mn in $CdAl_2O_4$ unit cell. During the geometry optimization, the atomic positions were optimized. The cutoff energy was 480 eV, and Brillouin zone integration was represented using the K point sampling scheme of a 5×5×5 Monkhorst–Pack grid. The convergence tolerance for geometry optimization was 5.0×10^{-6} eV per atom, the maximal ionic Hellmann–Feynman force was 1.0×10^{-2} eV $Å^{-1}$, the stress tensor was 2.0×10^{-2} GPa and the maximal displacement being within 5.0×10^{-4} Å.

Table S1. Optimized structural parameters of $CdAl_2O_4$ obtained from the Geometry Optimization.

Element Symbol	Mult. Wyck.	x/a	y/b	z/c
Cd1	18f	0.20085	0.17768	0.24733
Al1	18f	0.21058	0.19950	0.58281
Al2	18f	0.21741	0.19911	0.91728
O1	18f	0.34060	0.34362	0.25124
O2	18f	0.22125	0.11287	0.04551
O3	18f	0.21775	0.11774	0.45330
O4	18f	0.18963	0.13848	0.74960

[a] a=b=14.2150 , c=9.5700 , α=β=90°, γ=120°, V=1674.70 $Å^3$ Space group R-3

Table S2. Refined structural parameters of $CdAl_2O_4$:0.03Mn^{2+} obtained from the Rietveld refinement.

Element Symbol	Mult. Wyck.	x/a	y/b	z/c	S.O.F.	U(Å^2)
Cd1	18f	0.20600	0.18360	0.24629	0.972	0.0089
Mn	18f	0.20600	0.18360	0.24629	0.028	0.0900
Al1	18f	0.20835	0.19826	0.5832	1.000	0.0040
Al2	18f	0.2179	0.19712	0.9165	1.000	0.0096
O1	18f	0.3427	0.3457	0.2575	1.000	0.0065
O2	18f	0.2201	0.1110	0.0474	1.000	0.0008
O3	18f	0.2147	0.1200	0.4480	1.000	0.0219
O4	18f	0.1934	0.1377	0.7463	1.000	0.0163

[a] a=b=14.219 , c=9.5718 , α=β=90^o, γ=120^o, V=1675.59 Å^3, Space group R-3, R_{wp}= 6.98%, R_{exp}=5.42%, χ^2= 1.800.

Figure S1

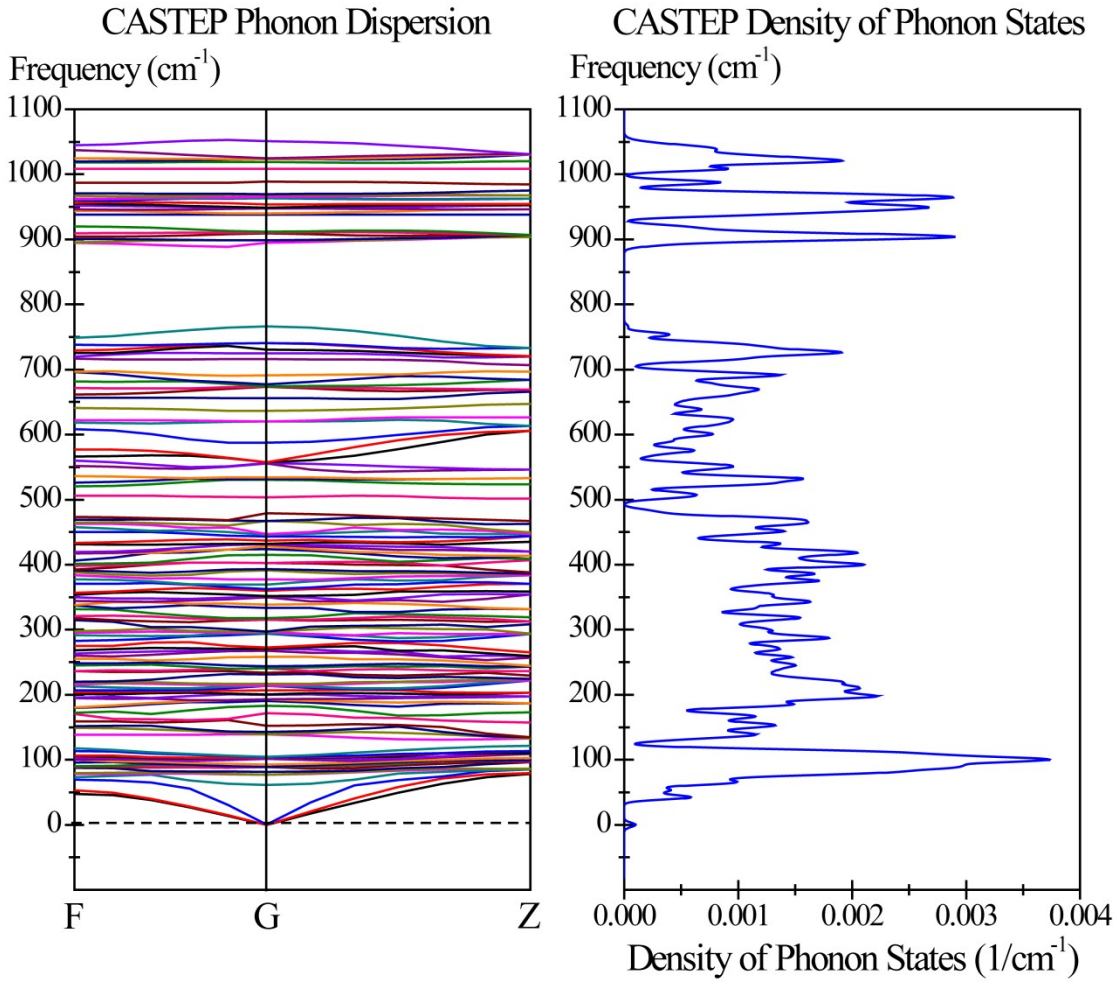

Fig. S1 Calculated phonon dispersion and density of phonon states curves.

Figure S2

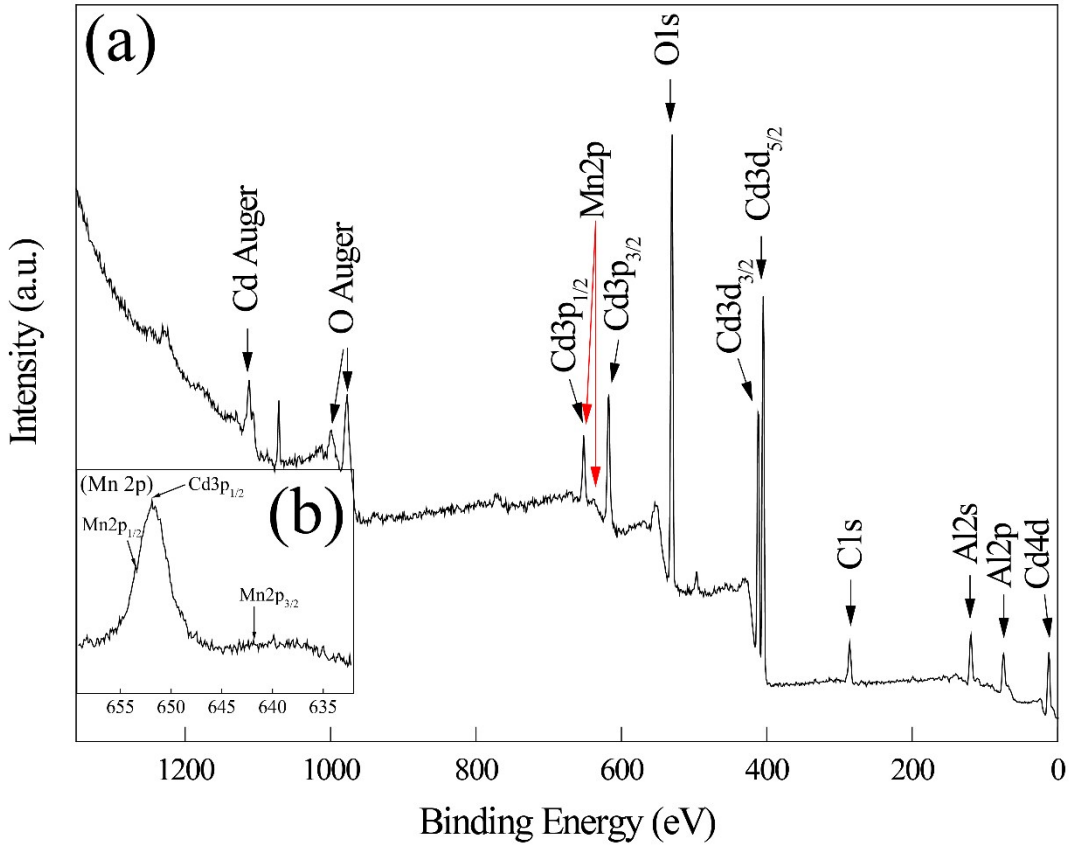

Fig. S2 XPS Spectrum of $CdAl_2O_4$:0.01Mn^{2+} (**a**) survey scan and (**b**) high-resolution scan of the Mn2p region.

Figure S3

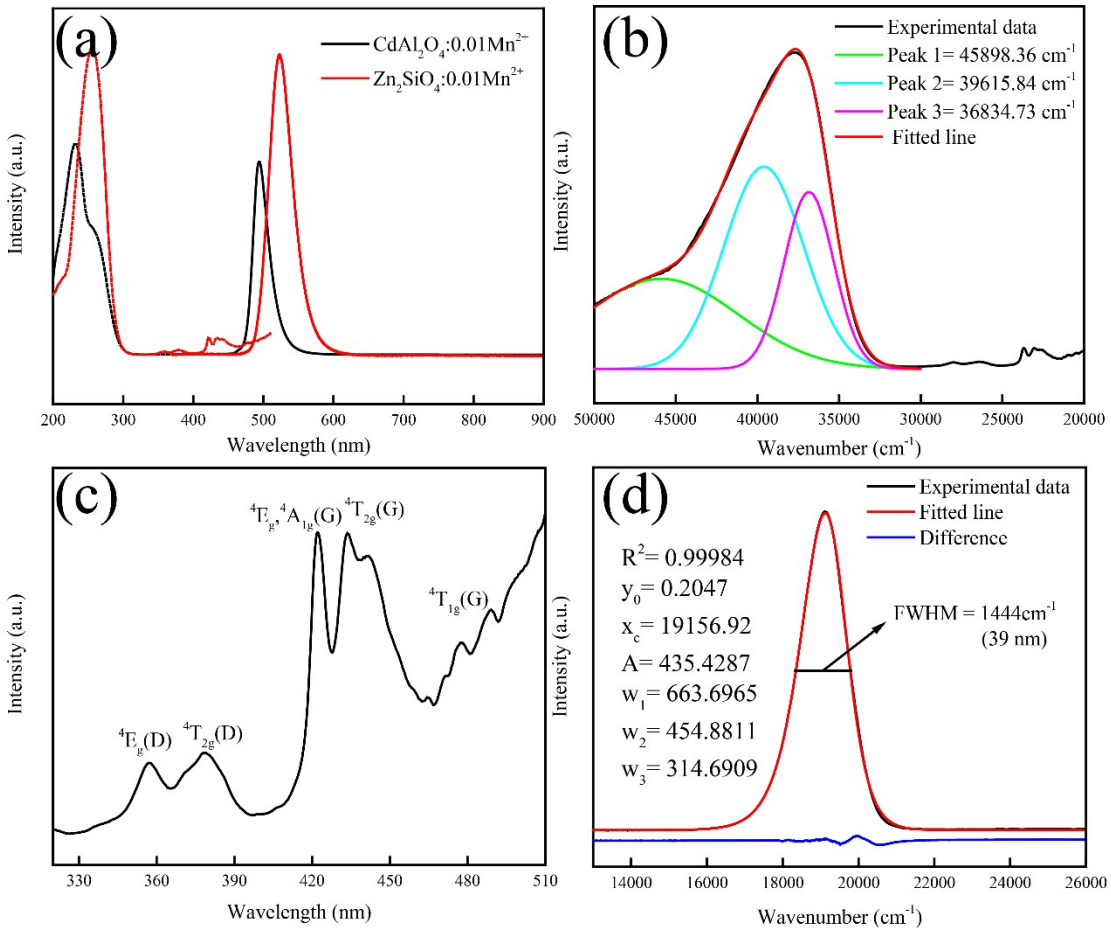

Fig. S3 Excitation and emission spectra of as prepared Zn_2SiO_4:0.01Mn^{2+} phosphor.

Figure S4

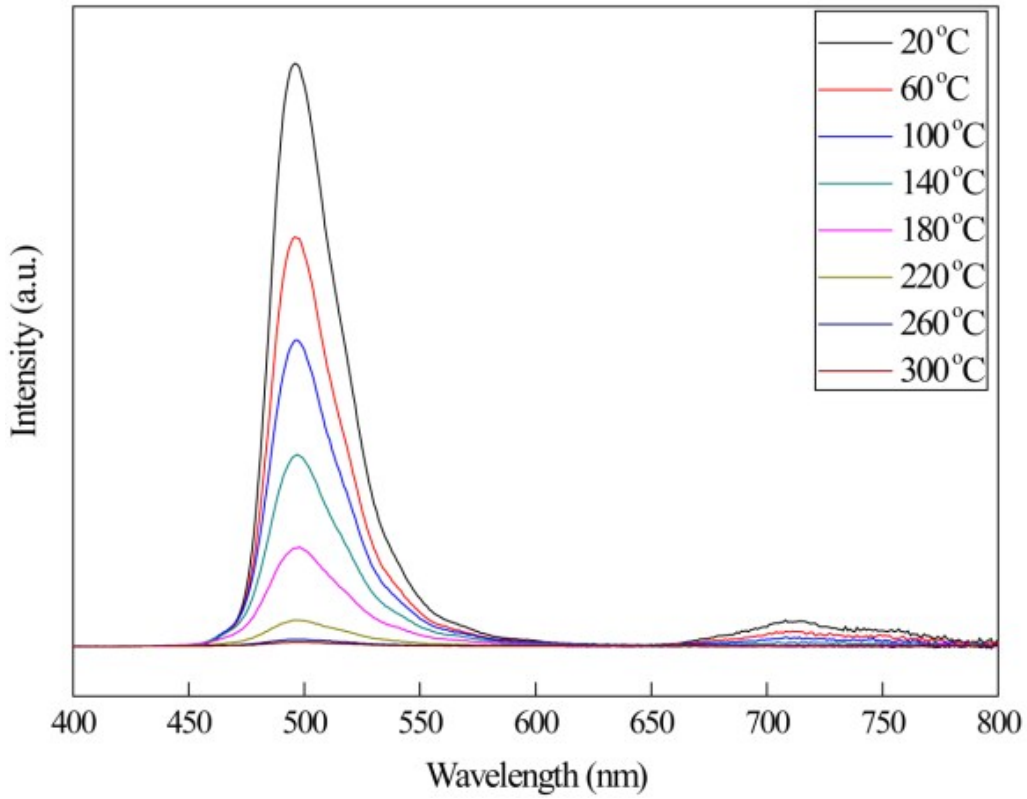

Fig.S4 The temperature-dependent emission intensity of the optimized $CdAl_2O_4$:0.015Mn^{2+} phosphor.

Figure S5

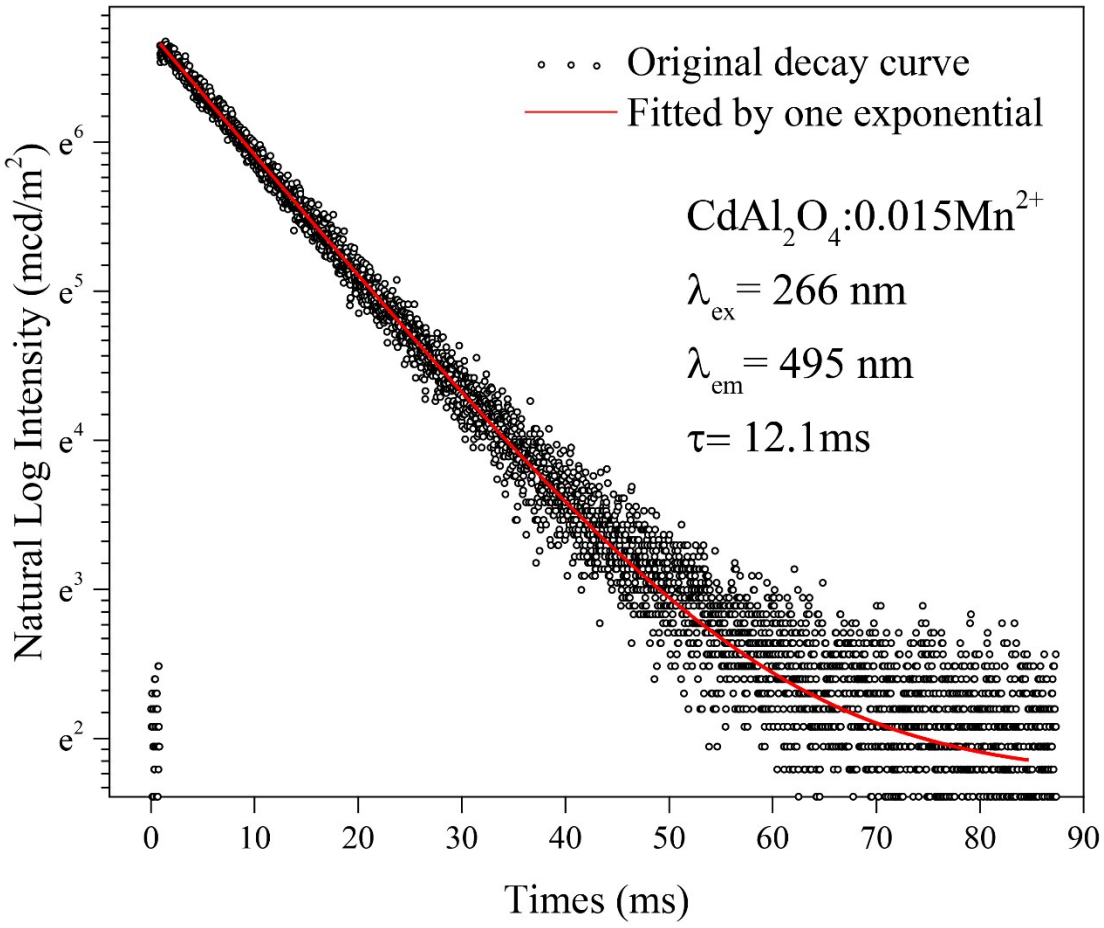

Fig.S5 Decay curves of Mn^{2+}-doped $CdAl_2O_4$ phosphor excited at 230 nm and monitored at 495 nm.

Figure S6

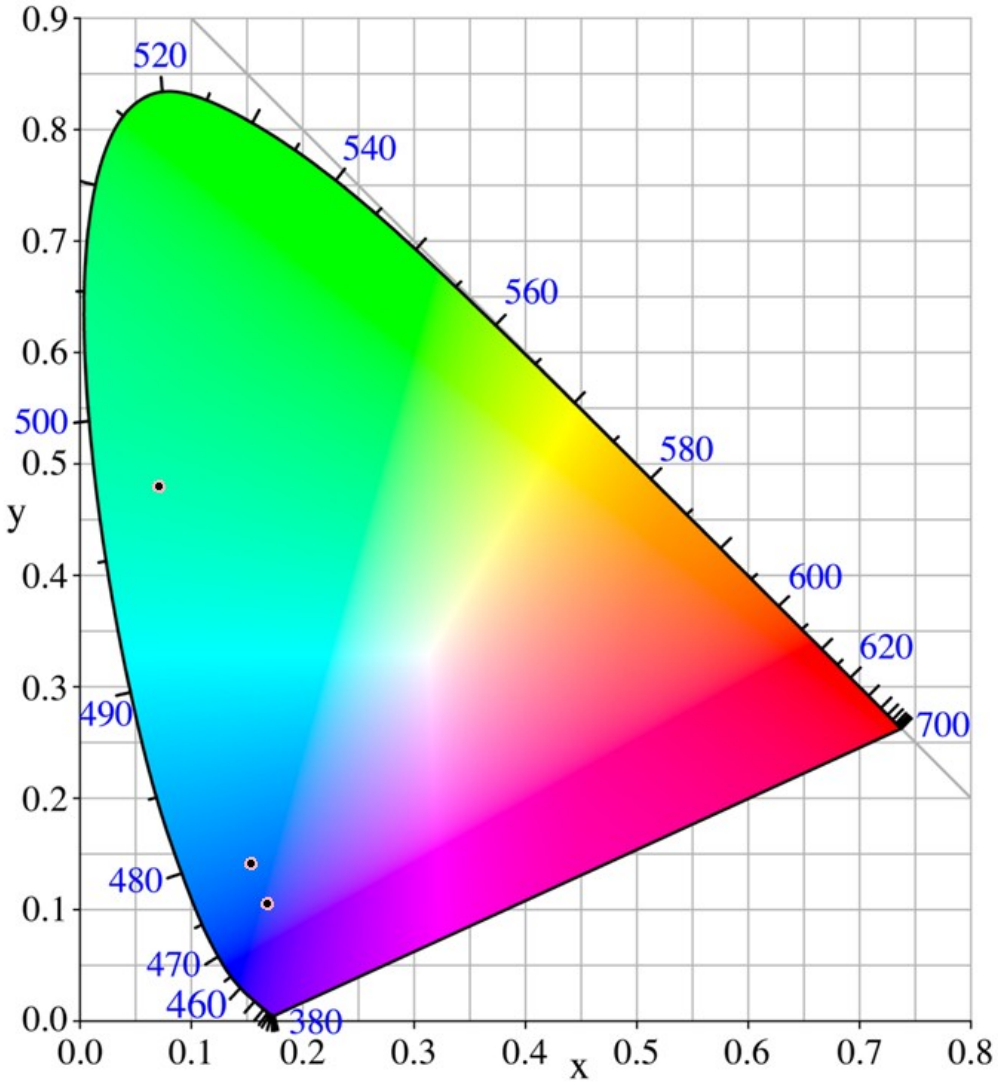

Fig. S6 CIE chromaticity diagram of $CdAl_2O_4$, $CdAl_2O_4$:0.0005Mn^{2+} and $CdAl_2O_4$:0.015Mn^{2+} phosphors excited at about 230 nm.

1. M. D. Segall, J. D. L. Philip, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *First-principles simulation: ideas, illustrations and the CASTEP code, J Phys: Condens Mat*. 2002, **14**, 2717.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Generalized Gradient Approximation Made Simple, Phys Rev Lett*. 1996, **77**, 3865-3868.