



Elucidation of Barocaloric Effect in Spin Crossover Compounds

Hend Salim Abdel Raof Shahed

Energie & Umwelt / Energy & Environment
Band / Volume 630
ISBN 978-3-95806-758-5

Forschungszentrum Jülich GmbH
Jülich Centre for Neutron Science (JCNS)
Quantenmaterialien und kollektive Phänomene (JCNS-2/PGI-4)

Elucidation of Barocaloric Effect in Spin Crossover Compounds

Hend Salim Abdel Raof Shahed

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment

Band / Volume 630

ISSN 1866-1793

ISBN 978-3-95806-758-5

Contents

1	Introduction	1
1.1	Motivation	1
1.2	Introduction to spin crossover	5
1.3	Polymorphism in spin crossover system	5
1.4	Cooperativity	6
1.5	Intermolecular interactions	7
1.5.1	Hydrogen bond	8
1.5.2	Van der Waals interactions	12
1.5.3	$\pi - \pi$ interactions	13
1.5.4	Intermolecular interactions in SCO compounds	15
1.6	Outline	17
2	Overview on Spin Transition	19
2.1	Spin transition nature	19
2.2	Factors influencing spin transition	20
2.2.1	Thermal cycling and scan-rate dependence	21
2.2.2	Pressure and magnetic field	21
2.2.3	Radiation of light	22
2.3	Detecting spin crossover behaviour	22
2.3.1	Magnetic measurements	23
2.3.2	X-ray diffraction	23
2.3.3	Differential scanning calorimetry and other techniques	25
3	Family of $[\text{Fe}(\text{PM-L})_2(\text{NCS})_2]$ Compound	27
3.1	$[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$	30
3.2	Effect of pressure on $[\text{Fe}(\text{PM-Bia})_2(\text{NCS})_2]$	33
4	Theoretical Background	35
4.1	Ligand field theory	35
4.2	Magnetization	42
4.3	Phase transition	45
4.3.1	Phase transition in spin crossover	49
4.3.2	Hysteresis	50
4.3.3	Volume compression and bulk modulus	51
4.4	Thermodynamic aspects	51
4.4.1	Thermodynamics of spin-crossover	53
4.4.2	Entropy driven spin crossover	54
4.4.3	Pressure driven spin crossover	55
4.5	Spin transition cooperativity	56

4.5.1	Non-interacting molecules	57
4.5.2	Domain model (Sorai and Seki model)	58
4.5.3	Solution model (Slitcher and Drickamer model)	59
5	Experimental Methods	63
5.1	Sample preparation	63
5.2	Magnetization	64
5.2.1	Methods and instruments	64
5.2.1.1	SQUID	64
5.2.1.2	PPMS Dynacool	66
5.2.2	Measurements	67
5.2.2.1	SQUID measurements	67
5.2.2.2	Dynacool measurements	68
5.3	Differential scanning calorimetry (DSC)	68
5.3.1	Methods and instruments	68
5.3.2	Measurements	69
5.4	Powder diffraction	71
5.4.1	Neutron powder diffraction	71
5.4.2	X-ray powder diffraction	72
5.4.2.1	In-house PXRD instrument	72
5.4.2.2	In-house measurement	73
5.4.2.3	Synchrotron measurement	73
5.4.3	Single crystal X-ray diffraction	74
5.4.3.1	In-house instrument	74
5.4.3.2	In-house measurement	75
5.4.3.3	Synchrotron single crystal diffraction	76
5.4.3.4	Synchrotron measurement	76
5.4.4	High pressure diffraction	78
5.4.4.1	Pressure determination	79
5.4.4.2	Synchrotron high pressure diffraction	81
5.4.4.2.1	P24 PETRA III	81
5.4.4.2.2	Measurement	81
6	Data Processing	83
6.1	Magnetization data	83
6.2	Differential scanning calorimetry	85
6.3	Powder diffraction data analysis	86
6.4	Single crystal X-ray diffraction data analysis	88
6.4.1	Data pre-processing	88
6.4.2	Searching, indexing, integration and data reduction	89
6.4.3	Structure solution and the phase problem	91
6.4.4	Structure refinement	93
6.4.5	Sequential processing of multiple temperature single crystal diffraction data set	94
6.5	High pressure single crystal X-ray diffraction	95
6.5.1	Pre-Processing: Conversion of XRD images with <i>CrysAlis Pro</i> software	95
6.5.2	Peak search	95
6.5.3	Indexing	95

6.5.4	Intensity integration	96
6.5.5	Structure solution and refinement	96
7	Results and Discussion	99
7.1	Magnetic properties: Effect of particle size and scan rate	99
7.2	Differential scanning calorimetry	103
7.2.1	Effect of thermal history	104
7.2.2	Effect of scan rate	107
7.3	Temperature-dependent powder X-ray diffraction	108
7.4	Temperature-dependent single crystal X-ray diffraction	109
7.4.1	Unit cell volume and lattice parameters	113
7.4.2	Intramolecular geometry	116
7.4.3	Intermolecular contacts	121
7.4.3.1	$\pi - \pi$ interactions	122
7.4.3.2	Van der Waals interactions	124
7.4.3.3	Hydrogen bonds	125
7.4.4	Intra and intermolecular changes impacting the lattice parameters anomalies	126
7.5	Mechanism of transition (Formation of domains)	128
7.6	Pressure-dependent crystal structure	131
7.6.1	Equation of state and anisotropic compressibility	132
7.6.2	Presence/Absence of HS-LS transition	133
7.6.3	High pressure in orthorhombic polymorph	138
7.6.4	Comparative analysis with previous studies	139
7.6.5	The role of intermolecular interaction for stiffness, compressibility, and transition	140
7.6.6	Comparison of high-pressure and low-temperature crystal packing	145
7.7	Thermal cycling	147
7.8	Effect of scan rate and intermediate state	151
7.9	Analysis of cooperativity and entropy change with Slichter and Drickamer model	154
8	Conclusion and Outlook	159
Bibliography		163
List of Figures		193
List of Tables		207
A Theory		215
B Measurement and Refinement Details		218
C Data processing		220
C.1	Least square approach	220
C.2	Processing of temperature-dependent single crystal x-ray data	221
C.2.1	Integration methodology for multiple data set	221

C.2.2	Sequential refinement of variable temperature diffraction data using SHELXL and seq_Shell Software	221
C.3	Processing of pressure dependent single crystal x-ray data	223
C.3.1	Conversion of XRD Images with the CrysAlisPro Software . .	223
C.3.2	Peak indexing for high pressure data	226
C.3.3	Data integration	227
C.3.4	Background evaluation	227
C.3.5	Outlier rejection	228
C.3.6	Data Reduction	228
D	Non-equilibrium kinetics for SCO	229
D.1	Non-isothermal kinetics of spin conversion	229
E		232
E.1	Effect of thermal cycling	232
E.2	Effect of different magnetic field	232
E.3	DSC measurements	235
E.4	Temperature-dependent crystal structure	236
E.5	Pressure-dependent crystal structure	244
E.6	Neutron	261

Energie & Umwelt / Energy & Environment
Band / Volume 630
ISBN 978-3-95806-758-5

Mitglied der Helmholtz-Gemeinschaft

