Pressure-induced photoluminescence in Mn²⁺-doped BaF₂ and SrF₂ fluorites

Ignacio Hernández and Fernando Rodríguez*

Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Facultad de Ciencias,
Universidad de Cantabria, 39005 Santander, Spain
(Received 27 September 2002; published 14 January 2003)

This work reports an effective way for inducing room temperature photoluminescence (PL) in Mn²⁺-doped BaF₂ and SrF₂ using high-pressure techniques. The aim is to understand the surprising PL behavior exhibited by Mn²⁺ at the cubal site of the fluorite structure. While Mn²⁺-doped CaF₂ shows a green PL with quantum yield close to 1 at room temperature, Mn²⁺-doped MF_2 (M=Ba,Sr) is not PL either at room temperature (SrF₂) or at any temperature (BaF₂) at ambient pressure. We associate the loss of Mn²⁺ PL on passing from CaF₂ to SrF₂ or BaF₂ with nonradiative multiphonon relaxation whose thermal activation energy decreases along the series CaF₂→SrF₂→BaF₂. A salient feature of this work deals with the increase of activation energy induced by pressure. It leads to a quantum yield enhancement, which favors PL recovery. Furthermore, the activation energy mainly depends on the crystal volume per molecule irrespective of the crystal structure or the local symmetry around the impurity. In this way, the relevance of the fluorite-to-cotunnite phase transition is analyzed in connection with the PL properties of the investigated compounds. The PL spectrum and the corresponding lifetime are reported for both structural phases as a function of pressure.

The photoluminescence (PL) properties of Mn²⁺-doped fluorites have been matter of great interest because of their relevance as scintillators, phosphors, and, in general, optical materials.[1–5] These doped crystals are attractive systems since Mn²⁺ occupies the cation site of the fluorite structure with eightfold coordination: complex MnF_8^{6-}.[1,6–10] This coordination leads to a crystal field at Mn²⁺, which is smaller than that attained in sixfold coordination like Mn²⁺-doped AMF_3 (A=alkali metal; M=divalent metal) fluoroperovskite systems. The crystal-field parameter $10Dq$ is about 0.5 and 1 eV for MnF_8^{6-} and MnF_6^{4-} complexes, respectively, and therefore is responsible for the green PL exhibited by Mn²⁺-doped fluorites and the red PL of Mn²⁺-doped fluoroperovskites.[1,11–13] Apart from the interest to synthesized blueshifted PL materials, Mn²⁺ green PL is attractive for studying nonradiative processes in isolated impurities since multiphonon relaxation phenomena are *a priori* less probable given that the number of phonons required to bridge the energy gap between the excited $^4T_{1g}$ state and the $^6A_{1g}$ ground state of Mn²⁺ in fluorites is almost twice than in the hexacoordinated complex. Besides, the $^4T_{1g} \rightarrow {}^6A_{1g}$ PL of the MnF_8^{6-} complex formed in Mn²⁺-doped CaF₂ at 2.48 eV (500 nm) exhibits the longest lifetime ever measured (τ=182 ms at 10 K) among the transition metal ions with a PL quantum yield close to 1 at room temperature (RT).[1,14] Unlike Mn²⁺-doped CaF₂, the MnF_8^{6-} complex formed in Mn²⁺-doped SrF₂ or BaF₂ is not PL either at RT or at any temperature at ambient pressure, respectively.[1,13,15] Although a red PL was observed in highly Mn²⁺-doped BaF₂ at low temperatures ($T<100$ K), however, it was not due to the isolated MnF_8^{6-} units, which were clearly identified by electronic paramagnetic resonance (EPR), but to BaMnF₄ precipitates.[15]

The surprising PL behavior exhibited by the MnF_8^{6-} complex along the fluorite series is noteworthy for investigating nonradiative processes on the basis of structural correlations since the local structure around Mn²⁺, as it was

derived from EPR,[8,15] is very similar is spite of the large lattice parameter variation: a=5.46 Å (CaF₂); 5.80 Å (SrF₂); 6.20 Å (BaF₂).[16] In fact, the estimated variation of Mn-F distance on passing from CaF₂ to BaF₂, $\Delta R_{Mn\text{-}F}$ =0.06 Å, is about an order magnitude smaller that the variation of the M-F distance undergone by the host crystal, $\Delta R_{M\text{-}F}$=0.32 Å, i.e., $R_{M\text{-}F}$ varies from 2.36 Å for CaF₂ to 2.68 Å for BaF₂.[15] These unusual long M-F (M=Ca, Sr, Ba) distances at the cation site contrast with the host bond-distance attained in AMF_3 perovskites whose M-F bond length varies from 1.99 Å for KMgF₃ to 2.26 Å for CsCaF₃,[11,12] hence the associated crystal field at the Mn²⁺ site fluoroperovskites is higher than in fluorites. This situation favors a blueshifted PL in fluorites according to the Tanabe-Sugano diagram for d^5 ions.[17]

The puzzling disappearance of Mn²⁺ PL along the fluorite series has been explained in terms of multiphonon relaxation processes whose activation energy strongly depends on the lattice parameter.[13,18,19] The larger the crystal volume, the smaller the activation energy; thus an increase of lattice parameter leads to a reduction of the PL quantum yield or even to PL quenching. The main goal of this work is just to investigate the inverse problem. It is whether pressure is able to transform these materials to PL systems and whether pressure-induced PL can be retained at ambient conditions after pressure release.

According to structural correlations established between the activation energy, E_a, and the crystal volume, V, in solid solutions of Mn²⁺-doped $Ca_{1-x}Sr_xF_2$,[18,19] the critical pressure required to induce PL in Mn²⁺-doped SrF₂ is about 2 GPa. With this pressure we would be able to fulfill the structural requirements to reach the lattice parameter (a_{PL} =5.75 Å) below which the crystal became PL. For BaF₂, however, this condition would be fulfilled by applying pressure above 30 GPa.

This paper reports PL spectra and lifetime measurements on Mn²⁺-doped SrF₂ and BaF₂ at RT using pressure spectroscopy. The aims are to explore whether pressure is able to
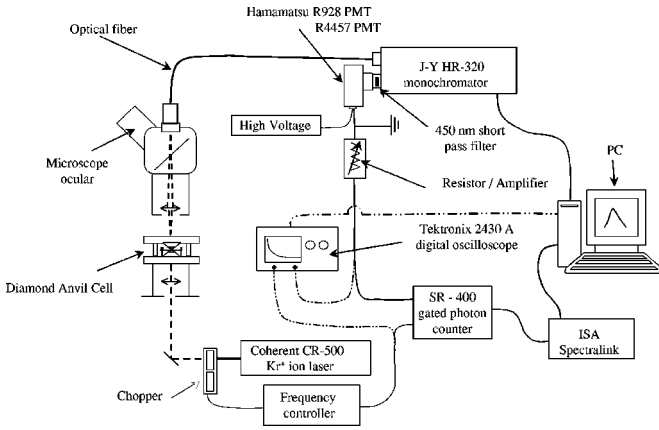
FIG. 1. Experimental setup for photoluminescence and lifetime measurements under pressure employed in this work. Time-resolved spectroscopy using photon counting techniques was required to detect the extremely weak PL signals attained in several samples at given conditions of pressure and temperature. Dotted wires represent the specific setup for lifetime measurements.

induce PL as well as the role played by this variable to control PL properties in these optical materials.

Single crystals of MF_2 ($M=$Ca,Sr,Ba) doped with Mn^{2+} (0.5% mol) were grown by the Bridgman technique as described elsewhere.[13,19] Saturation occurs for MnF_2 nominal concentrations higher than 0.3% in BaF_2.[20]

Hydrostatic pressure experiments were performed in a High Pressure Diamond Optics, Inc. Diamond Anvil Cell (DAC). An ethanol-methanol-water 16:3:1 mixture was used as pressure transmitter and the pressure was calibrated through the ruby PL. Single crystals of Mn^{2+}-doped SrF_2 and BaF_2 (typical dimensions: $100\times80\times40$ μm^3) were employed. PL spectroscopy was accomplished upon excitation into the $^4A_{1g}$; ^4E_g excited state of Mn^{2+} with the 407 nm

line of a coherent I-302-K krypton laser. Due to the extremely low PL quantum yield and lifetime ($\eta\approx0$; $\tau\approx0$ for both crystals at ambient conditions) we used a high-sensitivity PL setup for pressure spectroscopy whose sketch is shown in Fig. 1. In addition, these systems exhibit a weak PL even for high quantum yields given that the Mn^{2+} crystal-field excitations ($^6A_{1g}\rightarrow^4\Gamma_i$) are spin and parity electric-dipole forbidden (oscillator strength $\sim10^{-7}$),[1] thus leading to very weak absorption peaks and long lifetime decays. The DAC is placed in a microscope with a lens system that allows focalization with a spot size of 10 μm. PL is collected through a uv fused silica optical-fiber bundle ($\varnothing=1$ mm) attached to a HR320 Jobin-Yvon monochromator. The PL spectrum was obtained by time resolved spectroscopy using modulated excitation and photon-counting techniques. For lifetime measurements the PL decay was achieved with a Tektronix 2430 using suitable filters in order to improve the detection performance.

Figure 2(a) depicts the PL and the corresponding excitation spectra of Mn^{2+}-doped CaF_2 at RT and ambient pressure. The excitation spectrum consists of several crystal-field excitations within the Mn^{2+} d^5 configuration in cubal symmetry. The low crystal-field parameter derived from the Tanabe-Sugano diagram, $10Dq=0.5$ eV, in comparison to octahedral MnF_6^{4-} complexes ($10Dq=1$ eV),[11] is responsible for the green PL observed in fluorites [Fig. 2(a), (b)]. Although the PL lifetime decreases from $\tau=182$ ms at 10 K to 84 ms at 290 K [Fig. 2(b)], the PL quantum yield approaches to 1 in this temperature range. Nevertheless PL disappears upon heating above 1200 K as a consequence of thermal-activated nonradiative deexcitation from the $^4T_{1g}$ excited state. Its transition probability can be described by[1]

$$\tau^{-1}=\tau_{rad}^{-1}(T)+\tau_{nonrad}^{-1}(T)=\tau_{rad}^{-1}(T)+p\exp\left(-\frac{E_a}{kT}\right), \quad (1)$$
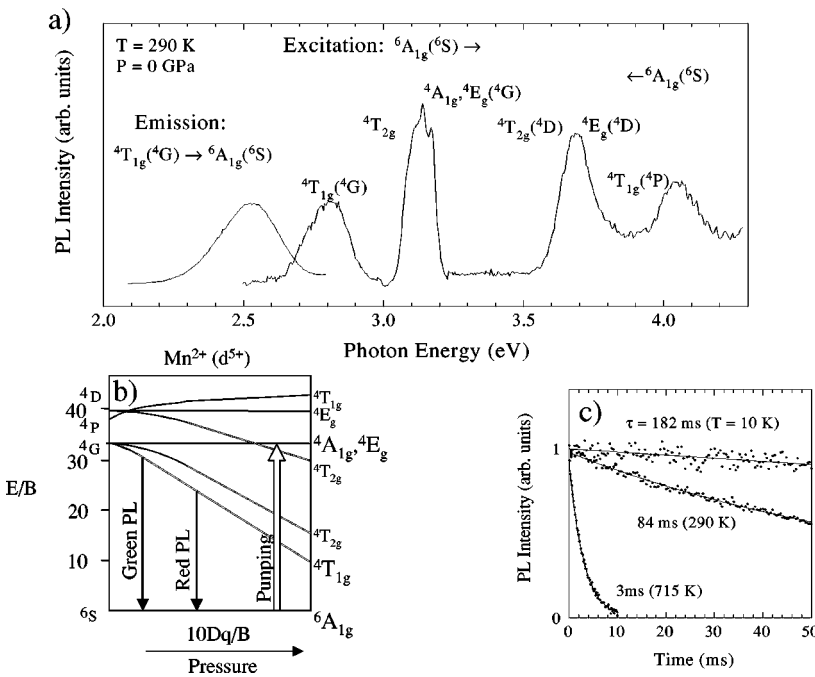

FIG. 2. (a) Emission and excitation spectra of Mn^{2+}-doped CaF_2: at ambient conditions. Bands are identified with the commonly used labels for cubal MnF_8^{6-} complex. (b) Tanabe-Sugano diagram for d^5 ions indicating the pumping state and the photoluminescence transitions for cubal MnF_8^{6-} (green) and octahedral MnF_6^{4-} (red) complexes. (c) Photoluminescence time dependence of Mn^{2+}-doped CaF_2 at different temperatures. The PL lifetime, τ, for a decay following $I(t)=I_0e^{-t/\tau}$ is indicated next to each decay curve.
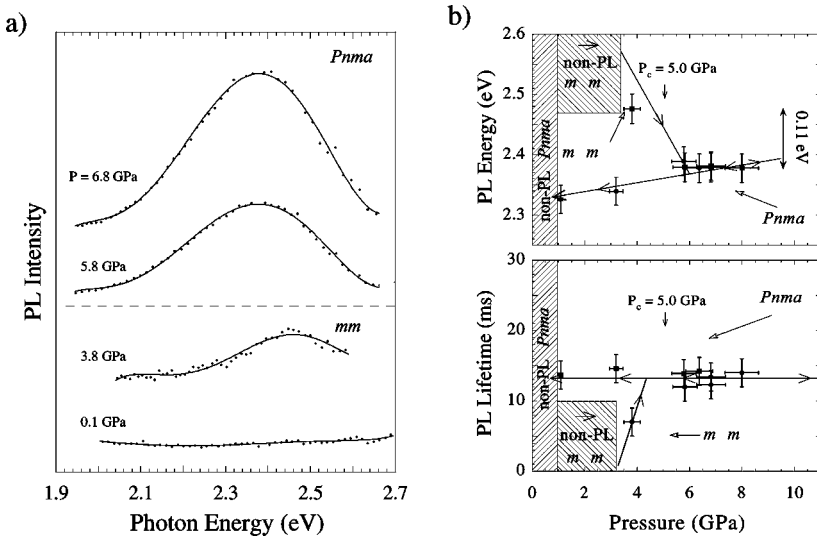
FIG. 3. (a) Variation of Mn^{2+}-doped SrF_2 PL spectrum with pressure at room temperature. The fluorite-to-cotunnite phase transition occurs at $P = 5.2$ GPa in upstroke. (b) Variation of the PL transition energy (top) and corresponding PL lifetime (bottom) as a function of pressure. Circles correspond to upstroke and squares to downstroke. Shaded areas represent zones where no PL was detected. Note the abrupt variations near the PT pressure.

where τ_{rad}^{-1} is the radiative transition rate and τ_{nonrad}^{-1} is the transition rate associated with nonradiative processes. E_a and p are the corresponding thermal activation energy and the associated preexponential rate, respectively, which strongly depend on the lattice parameter.[19] The competition between these two terms determines whether the system will be or will not be PL at given conditions of pressure and temperature.

Figures 3 and 4 show the pressure experiments carried out on Mn^{2+}-doped SrF_2 and BaF_2. Note that application of pressure in Mn^{2+}-doped SrF_2 favors the appearance of the green PL at 2.32 eV ($\tau = 8$ ms) above 3.8 GPa in agreement with expectations based on the reduction of τ_{nonrad}^{-1} due to the pressure-induced increase of E_a. Above this pressure there is a PL redshift of 0.11 eV [Fig. 3(b)], which is accompanied by an increase of both PL intensity and lifetime ($\tau = 14$ ms). Similarly to findings in Mn^{2+}-doped $Ca_{0.25}Sr_{0.75}F_2$,[18] we associate these changes with the occurrence of the fluorite-to-cotunnite structural phase-transition (PT), which takes place at 5.2 GPa in upstroke in SrF_2.[21,22] Interestingly, the cotunnite phase (orthorhombic $Pnma$),[16] and its associated PL, re-

mains upon downstroke. We still observed PL down to 1.0 GPa that roughly corresponds to the cotunnite phase due to the large PT hysteresis.[22] Nevertheless, below this pressure the system transforms back to the fluorite phase, thus preventing PL to occur at ambient conditions.

The observation of pressure-induced PL at 4.8 GPa in Mn^{2+}-doped BaF_2 is noteworthy (Fig. 4). The PL band peaks at 2.19 eV and appears at a lower pressure than the estimated $P = 30$ GPa. The PL undergoes a redshift of 0.15 eV from 4.8 to 22 GPa [Fig. 4(b)] but the associated lifetime ($\tau = 18$ ms) hardly varies with pressure. The unexpected appearance of PL in Mn^{2+}-doped BaF_2 must be ascribed not only to structural changes around Mn^{2+} as a consequence of the fluorite-to-cotunnite PT at 1.7 GPa in upstroke,[21,22] but mainly to the important reduction of crystal volume of about 10% attained at the PT pressure.[23,24] In fact, if we assume that E_a relies mainly on the volume per molecule irrespective of the crystal structure either fluorite or cotunnite, then the change of volume attainable at PT would be large enough to reach the structural requirements for PL to occur at a pressure of 4.8 GPa. Therefore the increase E_a due to the PT
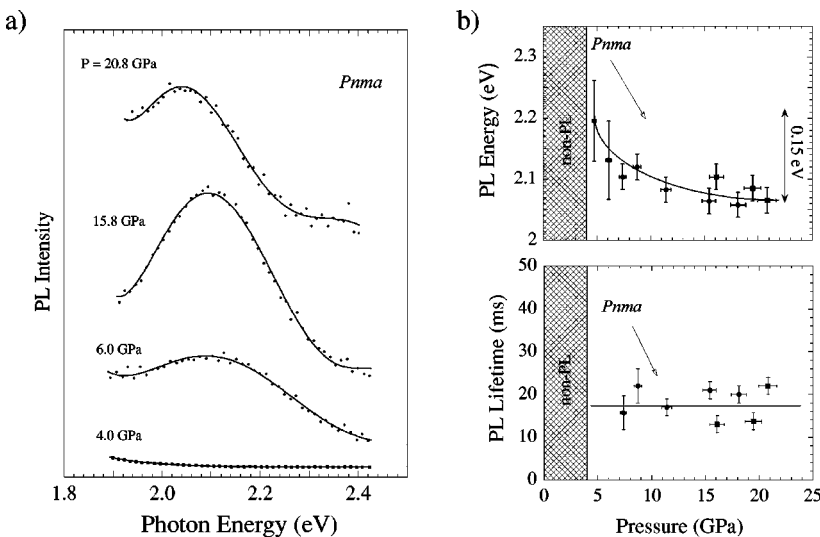

FIG. 4. (a) Mn^{2+}-doped BaF_2 PL spectrum as a function of pressure at room temperature. The PT takes place at $P = 1.8$ GPa. (b) Variation of the PL transition energy (top) and PL lifetime (bottom) with pressure. Shaded areas represent the pressure range where no PL was detected. Solid lines are guides for the eye. Note the redshift of 0.15 eV in Mn^{2+}-doped BaF_2 undergone by the PL band in the 0–22 GPa pressure range.

volume reduction $(V_{\mathrm{cotunnite}}/\mathrm{mol} \sim 0.9 V_{\mathrm{fluorite}}/\mathrm{mol})^{23,24}$ and subsequent increase of pressure fulfill the condition $\tau_{\mathrm{nonrad}}^{-1} \lesssim \tau_{\mathrm{rad}}^{-1}$ and hence radiative deexcitation becomes dominant. In downstroke, the PL gradually decreases and disappears below 4.8 GPa.

Unlike volume reduction within the fluorite structure ($Fm3m$ phase), which is responsible for the pressure-induced PL in Mn^{2+}-doped SrF_2, the main mechanism for PL recovery at RT in these systems is the occurrence of the structural PT. In Mn^{2+}-doped BaF_2, PT provides the structural requirements for PL at moderate pressures ($P = 4.8$ GPa versus the estimated $P = 30.0$ GPa). Interestingly, these systems present a large pressure hysteresis, $\Delta P \approx 2$ GPa.[21] Although this hysteresis is insufficient to retain the cotunnite phase ($Pnma$) at ambient pressure after downstroke in SrF_2, it achieves this phase in BaF_2.[21] The stabilization of the cotunnite phase at ambient pressure is a consequence of the low critical pressure of BaF_2 in upstroke, $P_C = 1.8$ GPa.[24] This result is noteworthy since it opens alternative ways for discovering more efficient PL materials on the basis of high-pressure phases which can be stabilized at ambient conditions. Furthermore, the experimental findings strongly support that the nonradiative process, which is responsible for the absence of Mn^{2+} PL in SrF_2 and BaF_2 at ambient conditions, mainly relies on the crystal volume. This result agrees with empirical observations in impurity-related PL materials stating that the smaller impurity host site, the more efficient PL material.[25]

We have shown that (1) the PL properties in impurity systems can be efficiently governed by pressure. In particular, the Mn^{2+}-doped SrF_2 and BaF_2 systems become PL upon pressure at RT. (2) The Mn^{2+}-doped fluorites MF_2 ($M =$ Ca, Sr, Ba) are ideal systems for studying nonradiative phenomena. The PL quantum yield varies from 1 to 0 on passing from $M =$ Ca to either Sr or Ba, and an analogous behavior is observed for the PL lifetime. This situation can be partially reversed by pressure, which modifies E_a. (3) The pressure-induced PT has revealed the cotunnite phase as an efficient PL structure. Moreover, the large PT hysteresis favors stabilization of this phase at ambient pressure, thus providing new ways for improving PL materials on the basis of high-pressure transformations. A complete spectroscopic study carried out on the whole crystal series as a function of pressure and temperature will be reported in a forthcoming paper.

---

*Author to whom correspondence should be addressed. Electronic address: rodriguf@unican.es

[1] P. A. Alonso and R. Alcalá, J. Lumin. **22**, 321 (1981).

[2] P. Schotanus, P. Dorenbos, C. W. E. Van Eijk, and H. J. Lamfers, Nucl. Instrum. Methods Phys. Res. A **281**, 162 (1989).

[3] R. Visser, P. Dorenbos, C. W. E. van Eijk, and H. W. den Hartog, J. Phys.: Condens. Matter **4**, 8801 (1992).

[4] R. Visser, P. Dorenbos, C. W. E. van Eijk, A. Meijerink, G. Blasse, and H. W. den Hartog, J. Phys.: Condens. Matter **5**, 1659 (1993).

[5] B. P. Sobolev, E. A. Krivandina, S. E. Derenzo, W. W. Moses, and A. C. West, in *Scintillator and Phosphor Materials*, edited by M. J. Weber, P. Lecoq, R. C. Ruchti, C. Woody, W. M. Yen, and R-y. Zhu, MRS Symposia Proceedings No. 348 (Material Research Society, Pittsburgh, 1994).

[6] R. J. Richardson, S. Lee, and T. J. Menne, Phys. Rev. B **4**, 1065 (1972).

[7] W. Gehloff and W. Ulrici, Phys. Status Solidi B **102**, 11 (1980).

[8] M. T. Barriuso and M. Moreno, Chem. Phys. Lett. **112**, 165 (1984).

[9] A. G. Badalyan, P. G. Baranov, V. S. Vikhnin, and V. A. Khramtson, Pis'ma Zh. Eksp. Teor. Fiz. **44**, 87 (1986) [JETP Lett. **44**, 110 (1986)].

[10] H. Soethe, V. A. Vetrov, and J. M. Spaeth, J. Phys.: Condens. Matter **4**, 7927 (1992).

[11] F. Rodríguez and M. Moreno, J. Chem. Phys. **84**, 692 (1986).

[12] M. C. Marco de Lucas, F. Rodríguez, and M. Moreno, Phys. Rev. B **50**, 2760 (1994).

[13] M. Díaz, F. Lahoz, B. Villacampa, R. Cases, B. Sobolev, and R. Alcalá, J. Lumin. **81**, 53 (1999).

[14] F. Rodríguez, H. Riesen, and H. U. Güdel, J. Lumin. **61**, 581 (1991).

[15] M. C. Marco de Lucas, M. Moreno, F. Rodríguez, and P. G. Baranov, J. Phys.: Condens. Matter **8**, 2457 (1996).

[16] R. W. G. Wycoff, *Crystal Structures* (Wiley, New York, 1963).

[17] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal ions* (Academic, New York, 1970).

[18] R. E. Gutiérrez, F. Rodríguez, M. Moreno, and R. Alcalá, Radiat. Eff. Defects Solids **154**, 287 (2001).

[19] F. Rodríguez, I. Hernández, R. E. Gutiérrez, S. García-Revilla, M. Moreno, and R. Alcalá, High Press. Res. **22**, 115 (2002).

[20] R. Alcalá (private communication).

[21] E. Yu Tonkov, *High Pressure Phase Transformations: A Handbook* (Gordon and Breach, Amsterdam, 1992), and references given therein.

[22] G. A. Kourouklis and E. Anastassakis, Phys. Rev. B **34**, 1233 (1986).

[23] J. Haines, J. M. Léger, F. Gorelli, D. D. Klug, J. S. Tse, and Q. Li, Phys. Rev. B **64**, 134110 (2001).

[24] G. A. Samara, Phys. Rev. B **2**, 4194 (1970).

[25] H. U. Güdel (private communication).