Unexpected value of transition pressure in the ionic layered BaFI compound observed by Raman scattering

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The high-pressure behavior of optical phonons in layered BaFI has been studied at ambient temperature using Raman spectroscopy up to 61 GPa. The pressure dependence of the zone-center phonons B_{1g}, E_g, and A_{1g} was measured in the tetragonal structure up to the phase transition near 55 GPa. The Grüneisen parameter of the low-frequency A_{1g} mode has a very large variation between 0 and 10 GPa. This evolution is attributed to a gradual layer-nonlayer transformation of the structure under pressure. For ionic compounds, and with respect to the classical hard-sphere model, phase transition tends to occur at about the same effective hard-sphere packing fraction. Consequently, the phase transition in BaFI could be thought to occur at a pressure lower than in BaFCl or BaFBr, in contradiction with our experimental data. Using thermodynamics arguments, the unexpected increase of the phase-transition pressure with increasing halogen size in $\mathrm{BaF}X(X=\mathrm{Cl}$, Br or I$)$ is attributed to the bidimensional characteristics of the structure, which is shown to expand the lattice volume and to decrease the internal energy by a polarization contribution U_{pol}.

I. INTRODUCTION

Layered materials have generated considerable interest since recent investigations have resulted in many remarkable achievements in semiconductors,[1] lubricants,[2] superconductors[3] or intercalation storages like graphyne[4] or fluorohalide (matlockite) compounds.[5] The generic chemical formula of matlockite family compounds is MFX where M is the metallic ion Ca, Sr, Ba, Pb or Eu, and X the halogen Cl, Br or I. The tetragonal structure of the fluorohalide crystals MFX has been shown to exhibit anisotropic compressibilities,[6] directly related to the observed macroscopic layered properties. Elastic anisotropy of typical layered crystals is known to be related to the existence of two distinct kinds of interatomic bonding: a covalent (or metallic) one inside the layers and van der Waals type forces between the sheets. In the case of MFX compounds, the layerlike conformation is quite surprising since these crystals are strongly ionic. In Ref. 6, based on x-ray-diffraction results, the stability of ionic MFX crystals in a layered structure is simply explained in terms of anisotropic Coulomb forces due to the asymmetric position of large polarizable halogen X atoms in their M_5 metallic pyramid cage (see Fig. 1). However, these assumptions still need to be confirmed by measurements carried out with a short-range order probe. The first part of the present work is devoted to the high-pressure Raman-scattering study of BaFI, one of the most layered fluorohalide crystal. This compound crystallizes at ambient conditions in the tetragonal structure $P4/nmm(D_{4h}^7)$. At the Γ point of the Brillouin zone, group theory predicts the existence of the following optical modes: $\Gamma_{opt}=2A_{1g}+B_{1g}+3E_g+3A_{2u}+3E_u$. A_{1g}, B_{1g}, and E_g modes are Raman active. The mode assignments of BaFCl, BaFBr, BaFI, PbFCl, PbFBr, and SrFCl at ambient conditions have been well established in the literature.[7–9] The atomic displacement patterns related to these modes have been described in Ref.

10. The mode labeled $A_{1g}(1)$ corresponds to the halogen motion along the c axis inside the M_5 pyramid whereas the other modes are related to the metallic tetrahedra breathing along $c[A_{1g}(2)]$, the fluor motion along c inside the M_4 tetrahedra (B_{1g}) and atomic motion along the a axis $[E_g(1,2,3)]$.

We also determined the transition pressure of BaFI and the second part of the discussion is devoted to the transition pressure trend with halogen size in ionic layered compounds. Actually, large X halogen atom size may induce chemical pressure due to steric effect, which has been experimentally confirmed for most ionic crystals. For $\mathrm{BaF}X$ compounds, because the Cl ion radius $(r_{Cl}=1.81$ Å$)$ is smaller than the Br one $(r_{Br}=1.96$ Å$)$, BaFCl at high pressure may be considered as analogous to BaFBr at ambient pressure.[11] Thus, one should expect a transition pressure for BaFBr lower than that for BaFCl. This conclusion is in disagreement with experimental results, where structural phase transition have been observed to occur at pressures near 21 and 27 GPa for BaFCl and BaFBr, respectively.[6,11–13] We confirm this unexpected result in the present work, where the phase transition of BaFI is shown to occur at a pressure far above 27 GPa.

II. EXPERIMENTS AND RESULTS

BaFI crystals were prepared by chemical reaction of BaF_2 and BaI_2.[14] For the high-pressure Raman experiments, the BaFI sample was cut as platelet from a colorless and transparent single crystal. The sample was about 30×20 $\mu\mathrm{m}^2$ in surface and 20 μm thick. Because BaFI is a layered compound, the faces perpendicular to the c axis are plane, parallel and as polished. The high-pressure cell was a membrane diamond-anvil cell (DAC).[15] A stainless-steel gasket was preindented to a thickness of 40 μm and a 150-μm-diameter hole was drilled in the center by spark erosion. Nitrogen was cryogenically loaded inside the DAC and used as a pressure transmitting medium. Pressure was systemati-
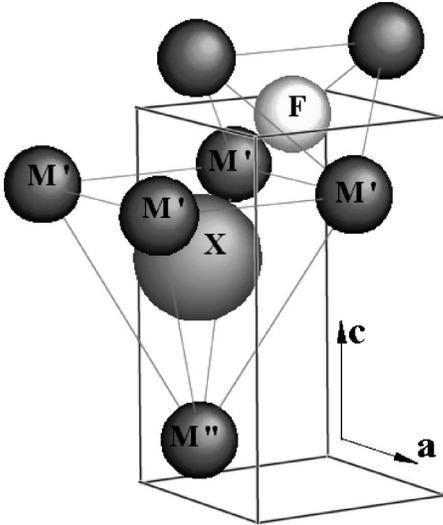
FIG. 1. Polyhedral representation of the matlockite structure. Contrary to the fluor inside the M_4 tetrahedron, the halogen X in the M_5 pyramid has an asymmetric coordination: X is equidistant from the four basal plane M' cations (distance $M'X$) but at a different distance from the M'' apex cation (distance $M''X$). For example, in BaFI, $d_{Ba'I}=3.582$ Å while $d_{Ba''I}=3.844$ Å.

cally measured before and after each Raman spectrum using the fluorescence emission of a ruby sphere[16] placed close to the sample into the gasket hole. The accuracy is better than 2 GPa at the maximum pressure reached (61 GPa). Raman spectra were excited with the 514.5-nm line of an Ar^+ laser focused down to 5 μm with a power level of about 50 mW at the entrance of the DAC. The scattered light was analyzed with a Dilor XY triple spectrometer and a liquid-nitrogen-cooled charge-coupled device multichannel detector. All spectra were recorded in the backscattering geometry with unpolarized light. The Raman frequencies were determined from a computer fit of the peaks with a Lorentzian profile. The accuracy is better than 1 cm^{-1}.

Before performing the high-pressure experiment, we examined the zone-center optical phonons of tetragonal BaFI at ambient conditions. We employed a large single crystal from which the micrometric sample used in the high-pressure experiments was extracted. With incident radiation parallel to the c axis, only A_{1g} and B_{1g} modes are allowed and clearly seen in the spectra (Fig. 2). However, because of defects, two of the three E_{1g} modes could also be observed in the spectra. The third E_{1g} peak [labeled $E_{1g}(1)$] could not be seen in the present work, neither with incident light parallel nor perpendicular to c. A simple comparison with phonon frequency of the same mode in BaFCl and BaFBr gives $E_{1g}(1)$ around 40 cm^{-1} for BaFI. The frequency assignment and a comparison with previous works are given in Table I.

The high-pressure experiment was carried out with incident light parallel to the tetragonal c axis. The B_{1g}, $E_g(3)$, $A_{1g}(1)$, and $A_{1g}(2)$ modes have been followed and the pressure dependence of their frequencies are shown in Fig. 3. The frequency of B_{1g}, $E_g(3)$, and $A_{1g}(2)$ modes increases with pressure and no anomaly occurs up to the transition pressure. The $A_{1g}(1)$ intensity gradually weakens under
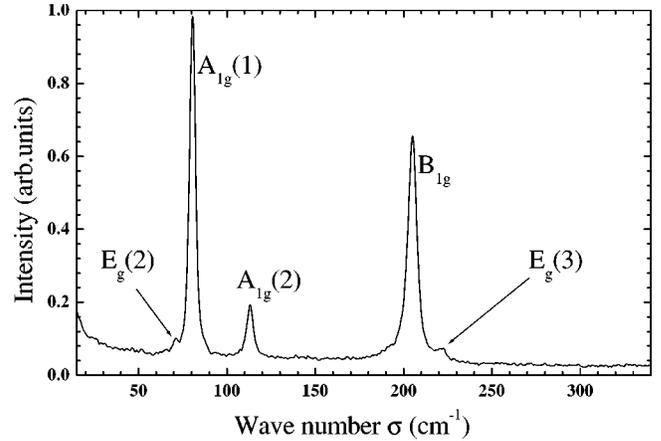

FIG. 2. Raman spectra of BaFI at ambient conditions.

pressure up to 30 GPa where the corresponding peak could not be seen anymore. Moreover, at low pressure, the frequency variation of this mode is considerable compared to others. The significance of this observation will be addressed in the Discussion.

At around 55 GPa, the vanishing of $E_g(3)$, the appearance of new peaks and the clear increase of the $A_{1g}(2)$ mode intensity reflect the onset of a structural transformation. These effects are enhanced after 24 h of relaxation at 61 GPa as shown in Fig. 4.

III. DISCUSSION

A. BaFI layered character under pressure

The mode Grüneisen parameters γ_i defined as $\gamma_i = -(d\ln\nu_i/d\ln V)_P$ have been calculated at different pressures. The isothermal Birch-Murnaghan equation of state was used to determine the pressure dependence of the unit-cell volume with $B_0=36$ GPa and $B'=6$.[6] Figure 5 shows a clear difference between the $A_{1g}(1)$ and the other modes. The Grüneisen parameter γ of $A_{1g}(1)$ varies strongly between 0 and ~10 GPa, which is characteristic of interlayer cohesive force evolution. Above 20 GPa, $\gamma[A_{1g}(1)]$ remains around 1, revealing a strengthening of the initial weak forces along the c axis. The atomic motion related to the $A_{1g}(1)$ optic mode is also shown in Fig. 5. Thus, the present data suggest that (i) the weak interactions inside the fluoride ha-

TABLE I. Raman-active BaFI Γ-point phonon frequencies (in cm^{-1}) at ambient conditions. The value of $E_g(1)$ frequency (superscript $\sharp$) has not been measured but estimated from a comparison with BaFCl and BaFBr modes.

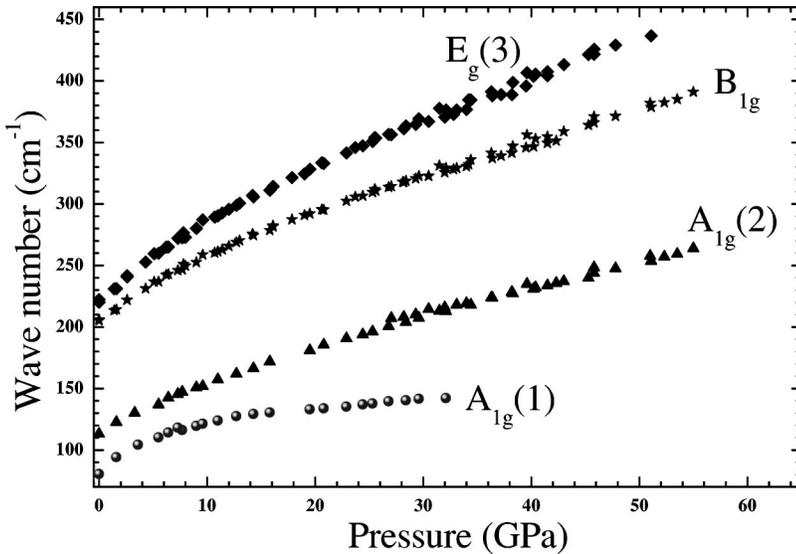| Mode	This work	Ref. 7	Ref. 17
B_{1g}	205	203	198
$A_{1g}(1)$	81		
$A_{1g}(2)$	113		
$E_g(1)$	$(40^\sharp)$		
$E_g(2)$	74		
$E_g(3)$	221	219	244

FIG. 3. Pressure dependence of the observed optical phonons in the tetragonal structure.

lides, MFX compounds, are localized between the XX double layers and (ii) the layered character disappears under pressure.

These results are in agreement with the assumptions made in Ref. 6. Briefly, the large polarizability and asymmetrical coordination scheme of the halogen atom have been shown to create large static dipoles on the anions, which stabilize the structure in a layerlike configuration. Under pressure the weak bonds are primarily affected. Therefore, the halogen is expected to move to a symmetric configuration, canceling the polarization of the X halogen. The pressure variation of the BaFX c/a ratio (determined by x-ray diffraction) is significant, while its value is pressure independent for the quasi-three-dimensional BaFCl compound ($c/a = 1.64$), the strong decrease from ambient pressure ($c/a = 1.71$) to about 15 GPa ($c/a = 1.64$) for BaFI is consistent with the present interpretation of a gradual layer-nonlayer transformation.

B. Transition pressure

Chemical substitution is often used to simulate pressure behavior. In BaFX family, the larger the ionic radius of the X halogen the larger is the local compactness (defined as the ratio between the X anion volume and that of the M_5 pyramid volume, see Fig. 1). In that sense, BaFI at ambient pressure could be thought as analogous to BaFCl or BaFBr at high pressure. Consequently, the phase transition of BaFI
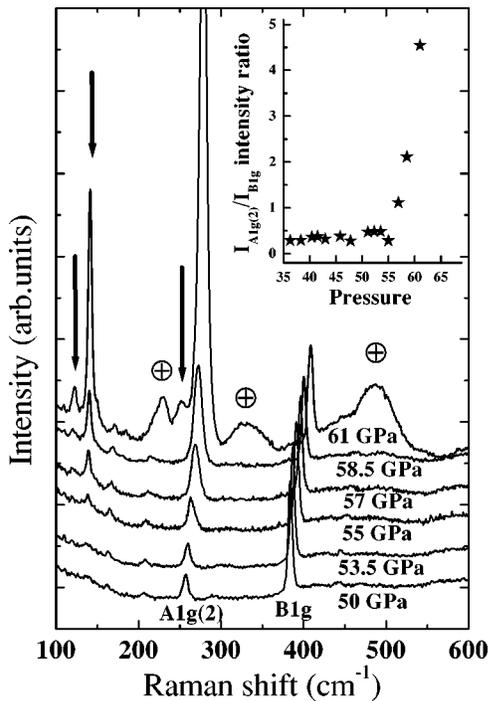

FIG. 4. Raman spectra of single-crystalline BaFI under different hydrostatic pressures in the neighborhood of the transition pressure. The spectra are shifted upwards for clarity. The upper spectrum has been recorded during 2×45 mn (2×5 mn for the other spectra) and after 24 h of relaxation at 61 GPa. The symbols $\oplus$ and the arrows point out nitrogen Raman modes and the new Raman peaks of the high-pressure phase, respectively. Inset: Pressure dependence of the intensity ratio between the $A_{1g}(2)$ and the B_{1g} peaks.
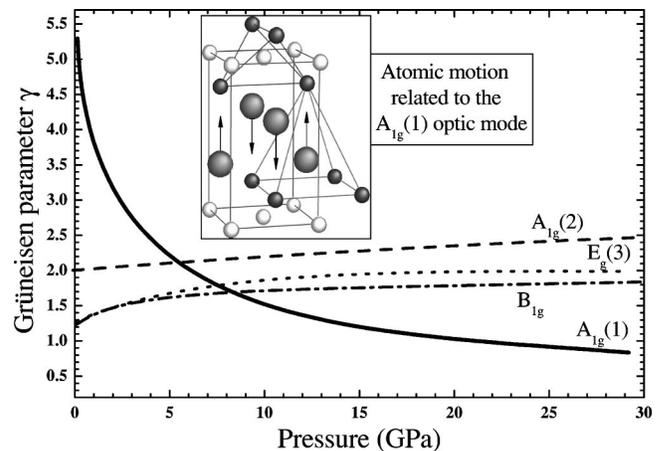

FIG. 5. Pressure dependence of the modes of Grüneisen parameters γ (left). The atomic motion related to the $A_{1g}(1)$ optic mode is also illustrated (inset).

TABLE II. Crystal data for BaFX compounds. V, a, and c are the experimental lattice volume and lattice parameters, respectively. c^{iso} and V^{iso} have been calculated using the experimental c/a of the quasi-three-dimensional crystal BaFCl. The difference $\Delta V = V - V^{iso}$ pictures the lattice expansion induced by the layerlike conformation.

Crystal	a(Å)	c(Å)	c/a	V (Å^3)	c^{iso} (Å)	V^{iso} (Å^3)	ΔV (Å^3)
BaFCl	4.394	7.225	1.64	139.5	7.225	139.5	0
BaFBr	4.508	7.441	1.65	150.9	7.385	149.7	1.2
BaFI	4.654	7.962	1.71	172.5	7.632	165.3	7.2

should be expected at lower pressure than in BaFBr or BaFCl. Experimentally and contrary to this simple representation, the tetragonal structure of BaFI appears to be extremely stable under pressure with $P_T = 55$ GPa. More generally, it is the behavior of the whole BaFX family, which contradicts the "classical" expectation since the transition pressure of BaFCl, BaFBr, and BaFI are 21, 27, and 55 GPa, respectively. Thermodynamic arguments can, however, be used to understand the experimentally observed elevation of the phase-transition pressure with increasing layered character in BaFX. Using the intuitive polarizable halogen model, effect of the bidimensional structure on the unit-cell volume and the internal energy of the crystal will be considered first.

1. Effect of the layer character on the unit-cell volume

In classical ionic structure, the value of the lattice parameters is only related to a simple steric effect. For example, in tetragonal structure the length changes of a and c with ion substitution are expected to be homothetic with a constant value of c/a. On the other hand, for bidimensional compounds with layers perpendicular to the c axis, as the MFX, the length of a is actually due to a steric effect, the weak bonds between the halogen planes increase the lattice parameter c leading to a layerlike conformation with a higher volume and higher c/a ratio as compared to the corresponding three-dimensional structure where only steric effect occurs, see Table II.

2. Effect of the layer character on the crystal energy

Because the electronic polarizability α is directly proportional to the atomic size, large size halogen anions (like iodine) are highly polarizable.[17] Combined with the halogen anisotropic coordination ($d_{M'X} \neq d_{M''X}$, see Fig. 1), these characteristics create a large static dipole on the halogen. The corresponding local electric field $\vec{E}$ gives an extra cohesive energy term U_{pol} to the three-dimensional lattice energy with $U_{pol} = -\frac{1}{2}N\alpha\vec{E}^2$ (N is the number of anions). Thus, a layered structure for ionic crystals with large halogen atoms appears to be the most favorable framework in terms of stability.

3. Thermodynamics of the phase transition

Thermodynamically, the equilibrium condition between two phases at temperature T is given by $P_T = -\partial F/\partial V|_T$,
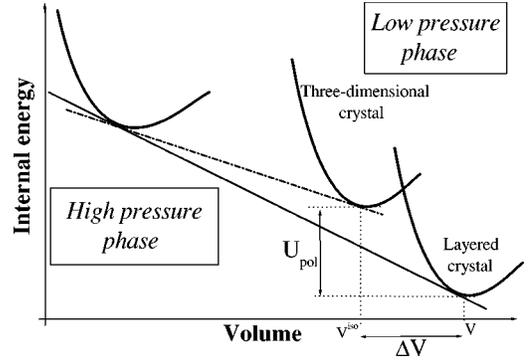

FIG. 6. Energy-volume curves for two- and three-dimensional MFX crystal. The offset of the high-pressure phase with respect to the tetragonal curves determines the phase-transition pressure. For crystals with highly polarizable halogen atoms like BaFI, the large value of $|\partial U_{pol}/\partial \Delta V|$ increases the stability pressure range.

where F is the Helmholtz free energy defined by $F = U - TS$ (U and S are the internal energy and the entropy, respectively). The entropy change at the transition has been ignored.[18] Thus, the pressure transition can be simply defined as the slope of the common tangent to both low- and high-pressure phases of $U(V)$ curves. In Fig. 6, the energy curve corresponding to the layered MFX structure is shifted with respect to a three-dimensional structure to lower energy (due to the U_{pol} term) and higher volume (by ΔV). As the two-dimensional character increases, the slope of the common tangent to the tetragonal and the high-pressure phase energy curves increases, and therefore the phase transition pressure increases.

IV. CONCLUSION

In this paper, we have examined the pressure variation of the optical-phonon frequencies in BaFI. The results suggest a gradual layer to three-dimensional evolution of the tetragonal structure under pressure. Moreover, the ambient pressure phase of BaFI appears to be extremely stable under pressure with a transition pressure of 55 GPa. This result shows that, doped with rare-earth ions, BaFI is potentially most interesting for technological applications as *in situ* pressure gauge for experiments with diamond-anvil cell.[19] In the high-pressure phase, three new peaks are observed, which is not contradictory with the proposed $P2_1/m$ space group.[13] We also attempted to understand why BaFI is more stable than BaFCl or BaFBr under pressure, in disagreement with the intuitive hard-sphere model. Taking into account the contribution of the polarization term due to the highly polarizable halogen atoms, a thermodynamic analysis allows us to answer this question. Finally, and from a more general point of view, the present study may also contribute to a better understanding of the chemical substitution effect origin on the critical temperature T_c of layered superconducting systems. As a matter of fact, the response of superconductors to pressure is important since a large pressure derivative dT_c/dP may be an indication that higher values of T_c should be reached through chemical substitution. Whereas this strategy has been successful for most cuprates (one of the most fa-

mous example has been given by Bednorz and Müller who induced high-T_c below 30 K in La_2CuO_4 by partial substitution of La by Ba[20]), it was also shown that chemical substitution and external hydrostatic pressure may have opposite effects on T_c.[21] On the other hand, our interpretation of the origin of chemical substitution effect (correlation with the polarization) is quite different from the one usually admitted for the superconductors (correlation with the atomic distances[22]), and may constitute an alternative (or additional) explanation.

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[1] T. J. Wieting and J. L. Verble, in *Electrons and Phonons in Layered Crystal Structures*, edited by T. J. Wieting and M. Schlüter (Reidel, Dordrecht, Holland, 1979), Vol. 3.

[2] E. Barrena, S. Kopta, D. F. Ogletree, D. H. Charych, and M. Salmeron, Phys. Rev. Lett. **82**, 2880 (1999).

[3] J. S. Schilling and S. Klotz, in *Properties of High-Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), Vol. 3.

[4] N. Narita, S. Nagai, and S. Suzuki, Phys. Rev. B **64**, 245408 (2001).

[5] Y. R. Shen, T. Gregorian, and W. B. Holzapfel, High Press. Res. **7**, 73 (1992).

[6] F. Decremps, M. Fischer, A. Polian, J. P. Itié, and M. Sieskind, Phys. Rev. B **59**, 4011 (1999).

[7] A. Rulmont, Spectrochim. Acta, Part A **30A**, 161 (1974).

[8] M. Sieskind and J. Morel, J. Solid State Chem. **144**, 339 (1999).

[9] J. F. Scott, J. Chem. Phys. **49**, 2766 (1968).

[10] F. Decremps, Thèse, Université Paris VI, 1998.

[11] H. P. Beck, J. Solid State Chem. **17**, 275 (1976).

[12] Y. R. Shen, U. Englisch, L. Chudinovskikh, F. Porsch, R. Haberkorn, H. P. Beck, and W. B. Holzapfel, J. Phys.: Condens. Matter **6**, 3197 (1994).

[13] N. Subramanian, N. V. Chandra Shekar, P. Ch. Sahu, Mohammad Yousuf, and K. Govinda Rajan, Phys. Rev. B **58**, R555 (1998).

[14] M. Sieskind, M. Ayadi, and G. Zachmann, Phys. Status Solidi B **136**, 489 (1986).

[15] R. Letoullec, J. P. Pinceaux, and P. Loubeyre, High Press. Res. **1**, 77 (1988).

[16] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[17] M. Sieskind (unpublished).

[18] G. Kalpana, B. Palanivel, I. B. Shameem Banu, and M. Rajagopalan, Phys. Rev. B **56**, 3532 (1997).

[19] Y. R. Shen, T. Gregorian, and W. B. Holzapfel, High Press. Res. **7**, 73 (1992).

[20] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).

[21] G. Nieva, S. Ghamaty, B. W. Lee, M. B. Maple, and I. K. Schuller, Phys. Rev. B **44**, 6999 (1991).

[22] A. A. R. Fernandes, J. Santamaria, S. L. Nakamura, J. Guimpel, and I. K. Schuller, Phys. Rev. B **44**, 7601 (1991).