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# Fermi Resonance Involving Non-linear Dynamical Couplings in Pb(Zr,Ti)O<sub>3</sub> Solid Solutions

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We have used first-principles-based simulations and Raman scattering techniques to reveal a novel dynamical phenomenon in Pb(Zr,Ti)O<sub>3</sub> solid solutions: a Fermi resonance (FR) emerging from the *non-linear* coupling between ferroelectric (FE) motions and tiltings of oxygen octahedra. This FR manifests itself as the doubling of a nominally-single FE mode in a purely FE phase, when the resonant frequency of the FE mode is close to the *first overtone* of the tiltings. We show that the FR is the result of a non-linear coupling that is proportional to the spontaneous polarization of the material, and derive an analytical model that captures the essence of the effect.

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Ferroelectrics (FE) form an important class of materials that has been used in many devices [1]. Several crucial properties of FE materials are solely due to electrical dipoles. These dipoles, however, are not the only degree of freedom in various FE compounds. For instance, antiferrodistortive (AFD) motions, that correspond to the tilting of oxygen octahedra, also exist in the technologically-important Pb(Zr, Ti)O<sub>3</sub> (PZT) solid solution [2–6]. Similarly, one of the most currently studied class of materials, namely multiferroics, also possesses magnetic dipoles [7]. Interestingly, the *coupling* between the electric dipoles and the other degree(s) of freedom can lead to novel effects of fundamental and technological interest. For instance, an additional peak of *E* symmetry emerges at low temperature in PZT systems because of FE and AFD interactions [4, 5, 8, 9]. Another example is electromagnons that manifest themselves as additional dielectric (or Raman) peaks in the GHz-THz regime in multiferroics [10–12]. These peaks occur only if the crystallographic phase is “doubly” ordered, e.g. if it possesses both a spontaneous polarization *and* long-range-ordered AFD or magnetic arrangement [13, 14]. One may wonder if novel dielectric or Raman peaks can also occur in FE *in case of a “singly” ordered phase*, e.g. if this phase only possesses a spontaneous polarization while the AFD motions do not adopt a long-range order (though existing locally). Determining the precise microscopic origin of such hypothetical novel peaks (if any) is also of obvious importance.

Here, we report that such phenomenon indeed exists in FE, via the combination of computational, theoretical and experimental techniques: two peaks of *A*<sub>1</sub> symmetry are found in PZT in the purely FE phase, when the resonant frequency of the *A*<sub>1</sub> mode is close to the resonant frequency of the *first overtone* of the AFD motions. Such previously overlooked doubling is a manifestation of Fermi resonance [15] involving *non-linear* couplings between FE and AFD motions.

We investigate the Pb(Zr<sub>0.47</sub>Ti<sub>0.53</sub>)O<sub>3</sub> (PZT) solid solution by using the effective Hamiltonian approach of Ref. [6]. In addition to homogeneous and inhomogeneous strains, this scheme has two degrees of freedom in each unit cell *i*: (1) the local soft mode displacement,  $\mathbf{u}_i$  (the product of  $\mathbf{u}_i$

with a Born effective charge  $Z^*$  is the electric dipole centered on the unit cell *i*); and (2)  $\boldsymbol{\omega}_i$  that characterizes AFD motion in the unit cell *i*. The direction of  $\boldsymbol{\omega}_i$  is the axis about which the oxygen octahedron tilts while its magnitude provides the angle of such tilting [6]. The total energy of the effective Hamiltonian approach consists of a sum of three terms  $E_{\text{tot}} = E_{\text{FE}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \eta_H, \{\sigma_j\}) + E_{\text{AFD}}(\{\boldsymbol{\omega}_i\}, \{\mathbf{v}_i\}, \eta_H, \{\sigma_i\}) + E_{\text{coupl}}(\{\mathbf{u}_i\}, \{\boldsymbol{\omega}_i\})$ , where  $\{\mathbf{v}_i\}$  are related to the inhomogeneous strain variables inside each cell,  $\eta_H$  is the homogeneous strain tensor, and  $\{\sigma_i\}$  characterizes the atomic arrangement, that is  $\sigma_i = +1$  ( $-1$ ) represents a Zr (Ti) atom sitting at the site *i*.  $E_{\text{FE}}$  and  $E_{\text{AFD}}$  gather the energetic terms solely involving the  $\mathbf{u}_i$  and  $\boldsymbol{\omega}_i$  degrees of freedom, respectively.  $E_{\text{coupl}}$  characterizes the interactions between FE and AFD motions and is given by:

$$E_{\text{coupl}}(\{\mathbf{u}_i\}, \{\boldsymbol{\omega}_i\}) = \sum_{i,\alpha,\beta,\gamma,\delta} D_{\alpha\beta\gamma\delta} \omega_{i,\alpha} \omega_{i,\beta} u_{i,\gamma} u_{i,\delta}, \quad (1)$$

where *i* runs over the unit cells and  $\alpha, \beta, \gamma, \delta$  denote Cartesian components – with the *x*-, *y*- and *z*-axes being chosen along the pseudo-cubic [100], [010] and [001] directions, respectively. The  $D_{\alpha\beta\gamma\delta}$  coefficients quantify the couplings between the FE and AFD motions. For symmetry reasons, only three different kinds of  $D_{\alpha\beta\gamma\delta}$  elements are non-zero and different from each other, namely  $D_{xxxx} = D_{yyyy} = D_{zzzz}$ ,  $D_{xxyy} = D_{yyxx} = D_{yyzz} = D_{zzyy} = D_{zzxx} = D_{xxzz}$  and  $D_{xyxy} = D_{yxxy} = D_{yzzy} = D_{zyzy} = D_{zxzx} = D_{xzxz}$ . These three kinds of coefficients are denoted by  $D_1$ ,  $D_2$  and  $D_3$ , respectively, hereafter.

We use  $12 \times 12 \times 12$  supercells (8,640 atoms) in which Zr and Ti atoms are randomly distributed to mimic disordered solid solutions. The effective Hamiltonian is then put into molecular dynamics simulations to obtain finite-temperature properties. For the chosen Ti composition of 53%, a cubic paraelectric phase is found for temperatures above  $\sim 800$  K and a *P4mm* tetragonal phase in which the polarization points along a  $\langle 001 \rangle$  direction exists between the Curie temperature  $T_C \sim 800$  K and another critical temperature  $\sim 120$  K. Such predictions agree well with experiments [2, 3, 16]. As in Ref. [6], a *I4cm* state is predicted to occur below  $\sim 120$  K. In

this state, the oxygen octahedra tilt, in a long-range fashion, about the same (001) polarization direction (with neighboring oxygen octahedra rotating in antiphase) – which is consistent with some recent measurements [6, 17]. The numerical scheme of Refs. [9, 18] is used to extract complex dielectric responses at different temperatures, and each peak found in the dielectric spectra is fitted by a classical harmonic oscillator  $\varepsilon(\nu) = S\nu_r^2 / (\nu_r^2 - \nu^2 + i\nu\gamma_r)$ , where  $\nu_r$ ,  $\gamma_r$  and  $S$  are the resonant frequency, damping constant, and oscillator strength of the oscillator, respectively.

Figures 1(a) and 1(b) display the real and imaginary parts of the *isotropic* dielectric response – i.e.,  $[\varepsilon_{xx}(\nu) + \varepsilon_{yy}(\nu) + \varepsilon_{zz}(\nu)]/3$  – of the studied PZT system versus frequency at 600 K and 400 K, respectively. The insets of such figures show the  $\varepsilon_{zz}(\nu)$  dielectric response, where  $z$  corresponds to the polarization’s direction. Figure 1(a) indicates that PZT behaves “normally” at 600K, i.e. it possesses a doubly-degenerate  $E$  mode at lower frequencies and a single  $A_1$  mode at higher frequencies. Note that the  $E$  (respectively,  $A_1$ ) mode corresponds to atomic vibrations perpendicular (respectively, parallel) to the direction of the spontaneous polarization. One important feature revealed by Fig. 1(b) is the “abnormal” existence of *two*  $A_1$  modes at 400K. These two modes are denoted as  $A_1^{(1)}$  and  $A_1^{(2)}$  in the following and their resonant frequencies are around 136 and 161  $\text{cm}^{-1}$ , respectively, at 400K. It is important to realize that the crystallographic phase is identical between 400 K and 600 K (that is,  $P4mm$ ). In other words, the doubling of the  $A_1$  modes is *not* associated with a phase transition, unlike the extra  $E$  mode that occurs at low temperature [9, 13]. Further simulations for PZT systems with different compositions in the morphotropic phase boundary (MPB), as well as using different supercell sizes, were also performed at 300 K and 400 K, and two  $A_1$  modes were also found there. This doubling of the  $A_1$  mode thus appears to be a general feature of PZT systems near their MPB. We also conducted additional simulations in which we switched off the *alloying* effects in PZT, that is, we treated the studied solid solution as a simple  $\text{Pb}\langle\text{B}\rangle\text{O}_3$  crystal for which  $\langle\text{B}\rangle$  represents a virtual atom that is intermediate between Ti and Zr atoms [19]. In that simplified case, the doubling of the  $A_1$  mode is still present at 300 K, which implies that such doubling has nothing to do with the presence of two B-atoms in PZT (Ti and Zr).

Interestingly, one Raman experiment [20] previously reported an active mode with a frequency of  $\simeq 125\text{cm}^{-1}$  while another infrared measurement indicated a resonant frequency around 160  $\text{cm}^{-1}$  at room temperature in  $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$  solid solution [21]. The fact that these two experimental frequencies are very close to our predictions strongly hints towards the possibility that one measurement determined the frequency of what we denoted as the  $A_1^{(1)}$  mode while the other measurement “saw” the  $A_1^{(2)}$  mode – with none of these two experiments realizing that two modes with  $A_1$  symmetry can exist in PZT at room temperature within the  $\simeq 100 - 170\text{cm}^{-1}$  range [33].

To better understand this unusual doubling of the  $A_1$  mode, Fig. 2 shows the temperature dependence of the resonant frequencies for the  $A_1$  peaks found in our simulations for  $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$ . Just below  $T_C$  and down to 525K, only a single  $A_1$  mode exists. The frequency of this mode follows there a square-root law, i.e.,  $\nu_r \sim |T_C - T|^{1/2}$ . On the other hand, for temperatures ranging between  $\sim 500\text{K}$  and  $\sim 100\text{K}$ , two modes of  $A_1$  symmetry exist, with the  $A_1^{(1)}$  (respectively,  $A_1^{(2)}$ ) mode having a frequency lower (respectively, higher) than that given by the square-root law. Furthermore, for temperatures below  $\sim 100\text{K}$ , the  $A_1^{(1)}$  and  $A_1^{(2)}$  modes merge into a *single* mode of  $A_1$  symmetry that follows again the square-root law. Figure 2 further reveals that the highest temperature at which the single  $A_1$  mode disappears in favor of the  $A_1^{(1)}$  and  $A_1^{(2)}$  modes is such as the frequency of this single  $A_1$  mode is nearly equal to *twice* the main resonant frequency associated with the antiphase AFD motions [34] (that are associated with the  $R$ -point of the first-Brillouin zone [9], i.e. with a zone-boundary phonon extending in the entire crystal). Such a feature is further confirmed by additional calculations in which the resonant frequency of the AFD motions is varied by hand, and strongly suggests that the coupling between the AFD and the soft modes is responsible for the doubling of the  $A_1$  mode. This latter possibility is consistent with the results of additional simulations in which we turned off the AFD motions or switch off the  $D_{\alpha\beta\gamma\delta}$  parameters of Eq. (1): in such cases, only a single  $A_1$  mode can be seen in the dielectric spectra down to the lowest temperature. We also numerically found that the  $D_2$  parameter has a stronger effect than the  $D_1$  coefficient on the doubling of the  $A_1$  modes, while the  $D_3$  parameter has merely no effect on such doubling. It thus appears that the doubling of the  $A_1$  modes mostly originates from an interaction between longitudinal FE displacement and transverse AFD motions.

The fact that the unusual  $A_1$  mode doubling requires an *overtone* of the AFD mode to be close to the resonant frequency of the single  $A_1$  mode points towards a *Fermi resonance* (FR) associated with *non-linear* couplings [15]. Such phenomenon is well known in molecules [22, 23], but much less documented in inorganic crystals, especially in perovskites [24–26]. Note that if the overtone of the AFD mode becomes too far away in frequency from the “bare” single  $A_1$  mode (that can be assumed to coincide with the fitted, square-root solid line of Fig. 2) then the FR cannot occur anymore. This explains the disappearance of the  $A_1^{(1)}$  and  $A_1^{(2)}$  modes in favor of a single  $A_1$  mode for temperatures below  $\sim 100\text{K}$ , as seen in Fig. 2.

In order to confirm and further understand the proposed FR, let us consider a structural phase that possesses a spontaneous polarization but in which the AFD  $\omega_i$ ’s do *not* organize themselves into a long-range order – exactly as in  $P4mm$  [35]. To simplify the investigation of the dynamics of  $u_i$  and  $\omega_i$  due to their non-linear couplings, we introduce  $\tilde{u}_i$  and  $\tilde{\omega}_i$  such as:

$$\begin{cases} \mathbf{u}_i(t) = \langle \mathbf{u} \rangle + \tilde{\mathbf{u}}_i(t) \\ \boldsymbol{\omega}_i(t) = \langle \boldsymbol{\omega} \rangle + \tilde{\boldsymbol{\omega}}_i(t) = \tilde{\boldsymbol{\omega}}_i(t) \end{cases}, \quad (2)$$

In the above equation,  $t$  represents time and  $\tilde{\mathbf{u}}_i$  (respectively,  $\tilde{\boldsymbol{\omega}}_i$ ) is the deviation of the local mode (respectively, AFD mode) in the unit cell  $i$  with respect to its spontaneous value  $\langle \mathbf{u} \rangle$  (respectively,  $\langle \boldsymbol{\omega} \rangle = 0$ ). Plugging Eq. (2) into Eq. (1), one finds that the essential FE-AFD non-linear coupling term that governs the dynamics of  $\tilde{\mathbf{u}}_i$  and  $\tilde{\boldsymbol{\omega}}_i$  has the following form (see Supplementary info):

$$H_{\text{coupl,dynam}} = \sum_i \kappa \langle u \rangle \tilde{u}_i (\tilde{\omega}_i)^2, \quad (3)$$

where  $\tilde{u}_i$  corresponds to the (small, dynamical and long-range correlated) motion along the polarization direction, and  $\tilde{\omega}_i$  corresponds to (small, dynamical and long-range correlated) AFD motions either perpendicularly to the polarization direction's (in that case, the  $\kappa$  parameter is related to the  $D_2$  parameter) or parallel to that direction (in that case,  $\kappa$  is proportional to  $D_1$ ). The dynamical equation for  $\tilde{u}_i$  is thus:

$$\frac{d^2 \tilde{u}_i}{dt^2} = -4\pi^2 (\nu_r^{\text{FE}})^2 \tilde{u}_i - \frac{\kappa \langle u \rangle}{m_u} (\tilde{\omega}_i)^2 + \frac{Z^* E(t)}{m_u}, \quad (4)$$

where  $\nu_r^{\text{FE}}$  is the frequency of the soft mode related to the derivatives of the aforementioned  $E_{\text{FE}}$  energy term, and  $m_u$  is the soft mode effective mass.  $E(t)$  is an applied *ac* electric field. Equation (4) further proves the existence of a coupling between the dynamical small (long-range correlated) displacement of the *square* of the AFD motion and the dynamical small (long-range correlated) displacement of the soft-mode in a polar phase, which is consistent with the proposed occurrence of FR involving AFD *overtone*. One can prove (see Supplementary info) that when  $\nu_r^{\text{FE}}$  is close to *twice* the AFD resonance frequency, Eq. (4) leads to *two* resonant frequencies for the  $A_1$  mode that are given by  $\nu_r^2 = \nu_{\text{FE}}^2 \pm \Omega^2$ , where  $\Omega^2$  depends on the  $\kappa$  coupling parameter, as well as, on the value of the spontaneous polarization. As Eq. (4) and  $\nu_r^2$  bear similarities to the analogous expressions for typical FR (see e.g., Ref. [27] and references therein), our simulations indeed predict that, as a consequence of the coupled dynamics of the FE and AFD modes, a FR occurs in PZT and manifests itself as the doubling of the  $A_1$  mode.

To experimentally confirm the predicted non-linear FR, we conducted Raman measurements on  $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  ceramics [36]. The sample was prepared by conventional mixed oxide routine using standard laboratory reagent grade starting powders (> 99.9% purity). Density of the sample was greater than 95% of its theoretical value. More details can be found in Ref. [16]. The Raman spectrum was obtained by exciting the optically polished sample with the 514.5 nm line from an Ar-laser at a power of 25 mW. The diameter of the laser spot on the sample surface amounted to 2-3  $\mu\text{m}$ , and the

power on the sample was about 5 mW. The spectral resolution was better than 2  $\text{cm}^{-1}$ . Raman spectra were recorded in a back-scattering geometry by a RM-1000 RENISHAW Raman spectrometer, equipped with a NExT filter to achieve the lowest frequency of 20  $\text{cm}^{-1}$ . The natural polarization of laser was used, which yields almost parallel polarization. The spectra, corrected from the instrumental function and from Bose-Einstein factor correction [28], were fitted with a sum of independent damped harmonic oscillators (modified Lorentzian shapes) using a home-made computer program. The spectrum at room temperature is shown in Fig. 3. As consistent with our simulations and other Raman experiments [29, 30], such spectrum reveals that (1) two modes are indeed necessary to fit well the data in the 120–180  $\text{cm}^{-1}$  range and (2) the resonant frequency of these two modes is close to twice the frequency of the AFD motions. The temperature dependence of these two experimental mode frequencies is also obtained (see figure 1 of the Supplementary info) and compares well with the simulation results depicted in Fig. 2.

In summary, computational, analytical and experimental tools have been used to report and understand the first FR involving the soft mode and an overtone of AFD motions in any FE – as a result of non-linear dynamical couplings. We thus hope that the present work enhances the current knowledge of ferroelectrics, dynamics and non-linear effects.

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- [33] Such overlooking of these two modes likely arise from the broadness and thus overlap of the  $A_1^{(1)}$  and  $A_1^{(2)}$  modes in Raman spectra. In this frequency range, there is also an  $E$  (LO) mode at  $\sim 110 \text{ cm}^{-1}$  (depending on temperature), which creates some confusion in the symmetry assignment of Raman peaks.
- [34] In fact, we found that there is another AFD resonant frequency, in addition to the main one shown in Fig. 2. For instance, at 500K, this second frequency occurs at  $105 \text{ cm}^{-1}$  versus  $58 \text{ cm}^{-1}$  for the main AFD frequency. Such second AFD frequency has a peak that is much weaker than the one associated with the main AFD resonant frequency, and is caused by alloy

effects. Note that, when using the virtual crystal approximation [19] to treat PZT, only one single AFD peak therefore exists and that two dielectric peaks of  $A_1$  symmetry also occur when twice the frequency of this single AFD mode is near the FE  $A_1$  frequency.

- [35] Note that the present FR occurs well within the stability range of the  $P4mm$  phase, which implies that phenomena that are strictly restricted to the vicinity of the ferroelectric phase transition are not fully relevant here.
- [36] Please see C. Ambrosch-Draxl and P. Knoll, Physica B, Volume 194-196, Part 2, 2091 (1994) and C. Ambrosch-Draxl, *Phase Separation in Cuprate Superconductors*, ed. E. Sigmund, (Springer, Berlin, 1994) for the issue about the existence of the FR effect on clusters of different sizes

### Captions:

Figure 1: (Color online) The isotropic dielectric response of  $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$  solid solution versus frequency, at 600 K (Panel a) and 400 K (Panel b). The insets show the  $\epsilon_{zz}$  dielectric response, where  $z$  corresponds to the direction of the polarization. Red and blue lines represent the real and imaginary parts, respectively, of such complex dielectric responses.

Figure 2: (Color online) Temperature dependence of the resonant frequency of the  $A_1$  modes and of twice the resonant frequency of the AFD mode in  $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$ . The black solid lines represents the fitting of the single  $A_1$  mode, for temperature above 525K, and its interpolation down to 0 K by a square-root law (i.e.,  $\nu_r \sim |T_c - T|^{1/2}$ ). The crystallographic ferroelectric phases of the system at different temperatures are also indicated.

Figure 3: (Color online) Room-temperature Raman Spectra of  $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  (corrected by the thermal population factor). The open symbols are the data, while the solid line represents their fit by the different peaks indicated (via dashed lines) at the bottom of the figure. Mode symmetries resulting from the effective medium approach detailed in Refs. [17, 31] are indicated above each peak. The residual difference between the data and the fit is indicated on the top of the figure, and is rather small – therefore emphasizing the need of having several harmonic oscillators to describe well the spectra. The dashed red lines represent the peaks associated with AFD,  $A_1^{(1)}$  and  $A_1^{(2)}$  modes.

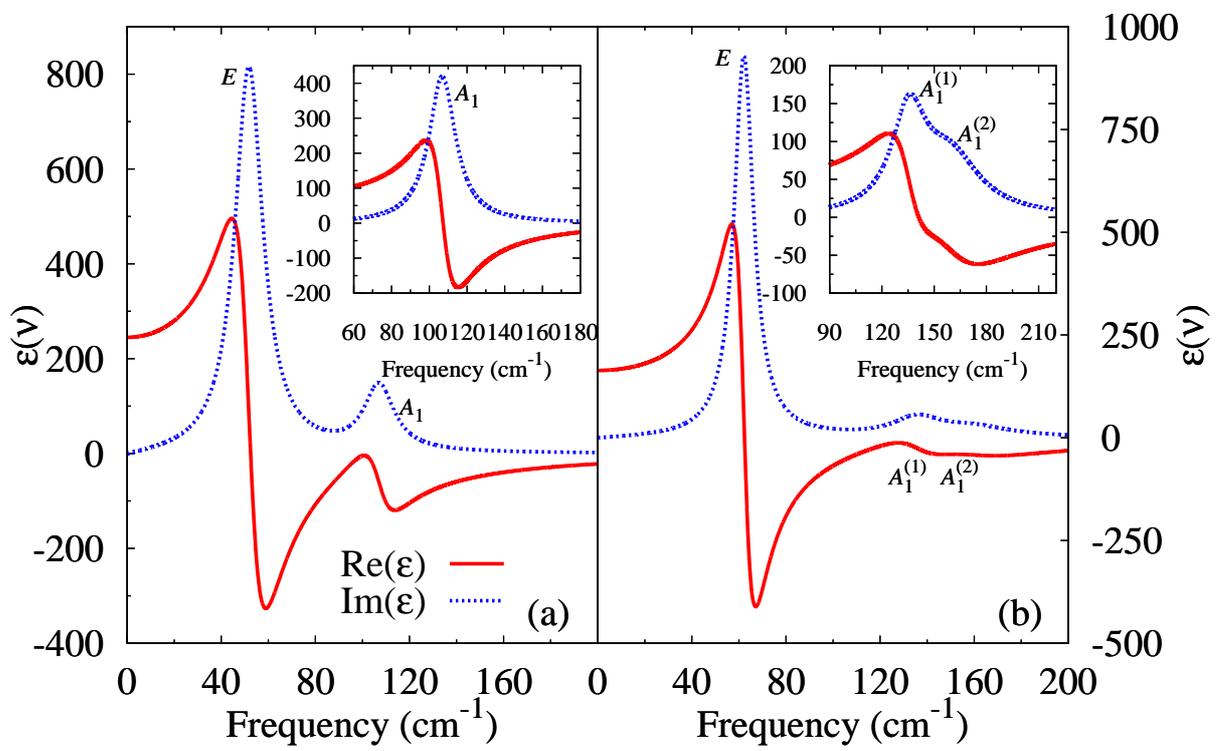


Figure 1 LF13472 07Sep2011

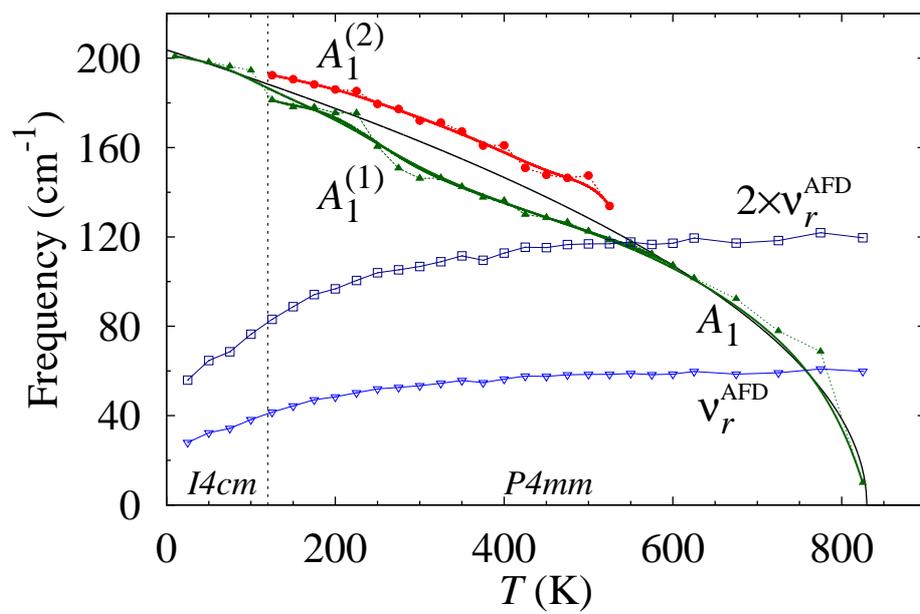


Figure 2 LF13472 07Sep2011

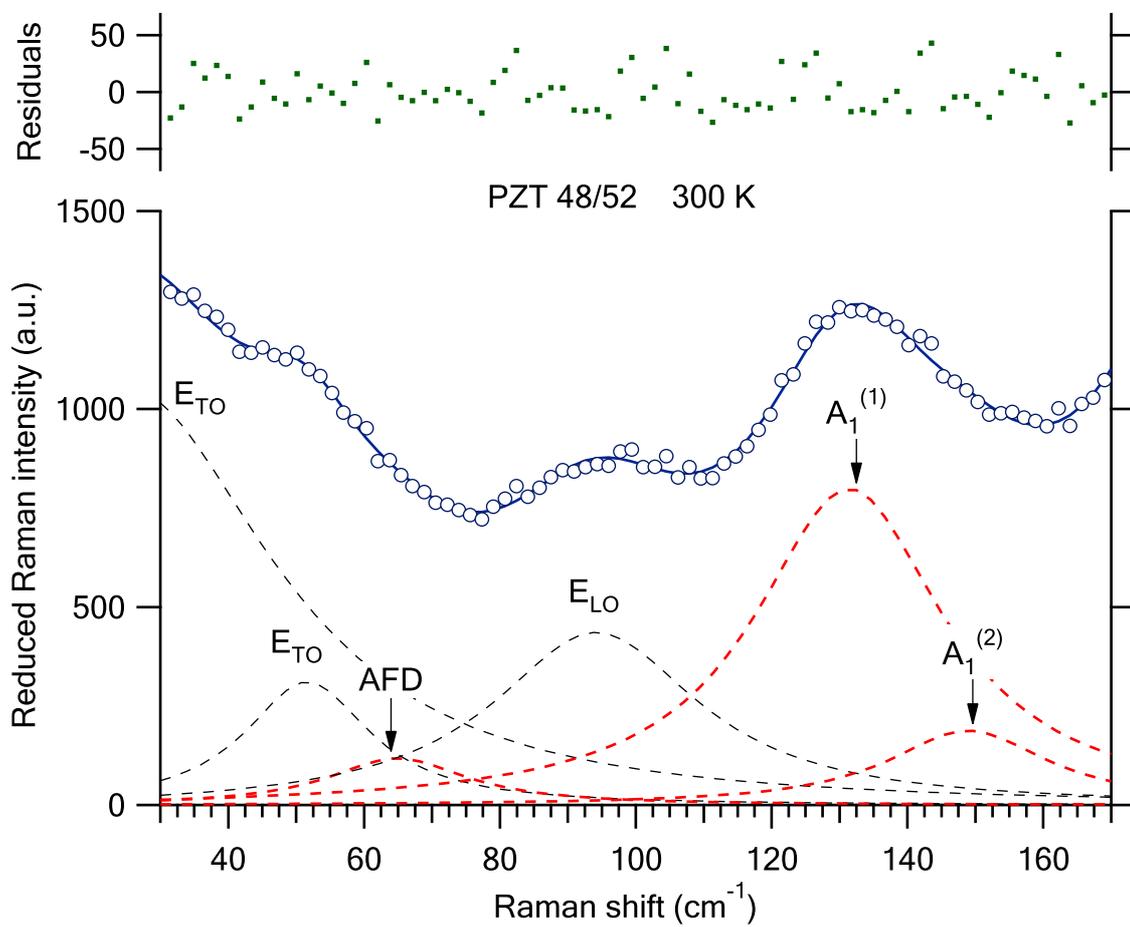


Figure 3 LF13472 07Sep2011