Raman intensities near second-order transitions: RP_5O_{14} ferroelastics (where R is a lanthanide)

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This paper provides a theory of Raman intensities for soft optic modes at second-order structural phase transitions. It combines the general theory of Fleury [Comments Solid State Phys. **4**, 167 (1972)], which gave expressions for the *total* light scattering cross section (including Raman, Brillouin, and central-mode components) with the theory of Errandonea [Phys. Rev. B **21**, 5221 (1980)], which described a specific form of coupling between the optic-mode order parameter Q and certain elastic strain components e_j for the RP_5O_{14} family of ferroelastics. The result of combining these two theories is a set of explicit expressions for the Raman intensities of the soft optic mode *alone* as a function of temperature, in both phases, and for all Raman tensor components. The predictions are compared with experimental data for both ZZ, YY, XX, and ZX polarizability components above and below T_c for both LaP_5O_{14} and TbP_5O_{14}; good agreement between theory and experiment is obtained.

I. INTRODUCTION

In 1972 Fleury provided[1] an analysis of light scattering near second-order structural phase transitions that related the total cross section to specific critical exponents. These cross-sectional dependences depend explicitly upon the form of coupling between the light and the order parameter. Unfortunately, however, the cross section in Fleury's theories are for total light scattered, including Raman, Brillouin, and "central-mode" intensities. It would be a significant advantage for experimentalists wishing to apply or test such theoretical formalism on their light scattering data to have an extension of these theories to predict the intensity dependence upon temperature for the Raman scattering alone, which in most cases is dominated by the T-dependent cross section of a single "soft" mode. In this paper we have combined Fleury's general results with a specific-mode coupling given by the free-energy description of Errandonea[2] for the lanthanide pentaphosphates, RP_5O_{14}, which exhibit $C_{2h}-D_{2h}$ ($P2_1/c$-$Pcmn$) displacive ferroelastic phase transitions for R = La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb.[3,4] The input parameters in applying this theory to our own data on LaP_5O_{14} and TbP_5O_{14} are optical phonon frequencies $\omega(T)$ as functions of temperature; these frequency measurements are, of course, completely independent of the measured intensities $I(T)$ and serve to guarantee that the theory is fully self-consistent.

We believe that this present work is therefore the first successful application of Fleury's theory to Raman intensities near second-order phase transitions, although for completeness we point out an earlier attempt by Worlock and Olson for the case of $SrTiO_3$.[5]

II. THEORY

It is already well established by dilatometric measurements,[2] Brillouin[2,6] and Raman studies,[3,4,7–9] and other techniques, that the eight lanthanide pentaphosphates that crystallize at room temperature in the C_{2h} point-group symmetry structure all undergo continuous transitions to a D_{2h} form at temperature between 120–180 °C and that these transitions can be described as mean field. The experimental light scattering studies of this system have been reviewed by Scott.[10] In the earlier studies some authors have noticed an obvious change in Raman intensities upon heating through the transition temperature,[4,8,9] but no quantitative analyses were given.

In a fixed scattering-experiment arrangement, the cross section of light scattering is determined by the Fourier component of the fluctuation in dielectric tensor:

$$\frac{d\sigma}{d\Omega} \propto \langle |e_s \Delta\mathcal{E}_{\mathbf{q},\omega} e_i|^2 \rangle \ . \tag{1}$$

In the case of a structural phase transition, the fluctuation of dielectric constant $\Delta\mathcal{E}$ arises from the fluctuation of the order parameter $\Delta\eta$. The coupling of η to $\mathcal{E}$ can be generally written as

$$\mathcal{E} = \mathcal{E}_0 + a\eta + b\eta^2 + c\eta^3 + \cdots \ . \tag{2}$$

If the linear term dominates the coupling, then

$$\langle |\Delta\mathcal{E}_{\mathbf{q},\omega}|^2 \rangle = a^2 \langle |\Delta\eta_{\mathbf{q},\omega}|^2 \rangle \ . \tag{3}$$

However, if the quadratic or cubic term becomes dominant, then

$$\langle |\Delta\mathcal{E}_{\mathbf{q},\omega}|^2 \rangle = 4b^2\eta^2 \langle |\Delta\eta_{\mathbf{q},\omega}|^2 \rangle \tag{4}$$

or

$$\langle |\Delta\mathcal{E}_{\mathbf{q},\omega}|^2 \rangle = 9c^2\eta^4 \langle |\Delta\eta_{\mathbf{q},\omega}|^2 \rangle \ . \tag{5}$$

$\Delta\eta_{\mathbf{q},\omega}$ is the Fourier transformation of the space-time correlation function of the order parameter. $\langle |\Delta\eta_{\mathbf{q},\omega}|^2 \rangle$ is generally called the dynamic structure factor. Based upon the fluctuation-dissipation theorem and the Kramers-Kronig relation and with the high-temperature approximation, Fleury expressed the dynamic structure factor $S(\mathbf{q},\omega)$ as

$$\frac{1}{kT}\int_{-\infty}^{\infty} S(\mathbf{q},\omega')d\omega' \propto \chi(\mathbf{q},\omega=0) , \tag{6}$$

where $\chi(\mathbf{q},0)$ is the generalized susceptibility. According to the critical behaviors of η and χ predicted by theory and to Eqs. (3)–(5), in the vicinity of transition point the light scattering intensity of the soft optic mode plus its coupled Brillouin and central modes is for linear coupling

$$\frac{I_1}{T} \propto \chi(\mathbf{q},0) \propto \epsilon^{-\gamma} , \tag{7}$$

quadratic coupling

$$\frac{I_2}{T} \propto \eta^2\chi(\mathbf{q},0) \propto \epsilon^{2\beta-\gamma} , \tag{8}$$

and cubic coupling

$$\frac{I_3}{T} \propto \eta^4\chi(\mathbf{q},0) \propto \epsilon^{4\beta-\gamma} , \tag{9}$$

where $\epsilon=(T-T_0)/T_0$. Simulations of Raman shift and intensity of soft optic mode versus temperature are shown in Fig. 1(a), where the mean-field exponents $\beta=0.5$, $\gamma=\gamma'=1.0$. It is obvious that for different coupling forms of η to $\mathcal{E}$ the intensity behaviors are different. For linear coupling the intensity decreases above and below T_c. For quadratic coupling the intensity is a step function, while in the case of cubic coupling the intensity decreases monotonically. In the two later cases the intensity expressions Eqs. (8) and (9) include factors of the order parameter η, therefore the light scattering intensity vanishes above T_c. From Eqs. (7)–(9) there are two possibilities of testing the validity of the theory: Firstly, to fit the exponential relation of Eqs. (7)–(9) and determine the critical exponents; secondly, to calculate the generalized susceptibility $\chi(\mathbf{q},0)$, which is an inverse second derivative of the free energy, and then to compare the explicit intensity expression with experiments. In the following we will deduce concrete expressions of $\chi(\mathbf{q},0)$ and light scattering intensity for RP_5O_{14} and carry out these two options.

The most remarkable spectroscopic features of the transition C_{2h}-D_{2h} in RP_5O_{14} are the total softening of elastic constant c_{55} and the limited softening of the lowest optic phonon A_g-B_{2g} (A_g in monoclinic C_{2h}, B_{2g} in orthorhombic D_{2h}). The phase-transition coupling is well revealed by the opto-acoustic coupling:[3]

$$c_{55}(T)=c_{55}(0)-\frac{D^2}{\omega_{T_0}^2(T)} , \tag{10}$$

where D is an opto-acoustic coupling constant. This relation indicates that a lattice instability can take place (i.e., $c_{55}=0$), even if the optic phonon retains a finite value. $\omega_{T_0}(T_c)$ is found to be 19–20 cm^{-1} for all monoclinic I crystals from LaP_5O_{14} to TbP_5O_{14}.[4]

Besides the A_g-B_{2g} soft mode, another soft mode of B_g-B_{3g} symmetry has also been reported.[4,9,10] It is thought to couple with elastic strain e_4. Because this soft mode's contribution to the phase transition is not significant, it is always ignored in the first step of consideration.

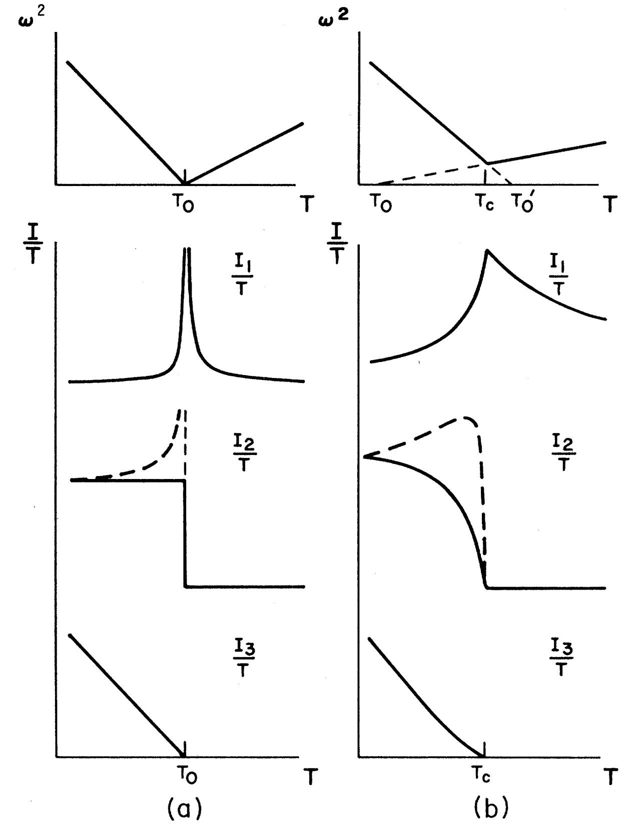

FIG. 1. (a) Mean-field-theory prediction of frequency square and light scattering intensity vs temperature for a uncoupled soft optic mode under different coupling forms of η to $\mathcal{E}$. Mean-field exponents are $\beta=0.5$ and $\gamma=\gamma'=1.0$, and are shown as solid curves; non-mean-field results using $\beta=\frac{1}{3}$ and $\gamma=\frac{4}{3}$ are shown as dashed curves for I_2. (b) Frequency square vs temperature curve and theoretically predicted intensity vs temperature curves for soft optic mode in RP_5O_{14} according to Table I. A linear coupling of form eQ and different coupling forms of η to $\mathcal{E}$ are assumed. Note that for I_2, non-mean-field exponents result in a nonmonotonic intensity dependence vs T as T_c is approached from below (dashed curve).

To describe the ferroelastic phase transition in RP_5O_{14}, Errandonea has suggested a phenomenological model of the free-energy expansion

$$F=F_q+F_e+F_c , \tag{11}$$

with

$$F_q=\frac{A}{2}Q^2+\frac{B}{4}Q^4 ,$$

$$F_e=\tfrac{1}{2}\sum_{i,j=1,3} c_{i,j}^0\cdot e_i e_j+\tfrac{1}{2}\sum_{k=4,6} c_{kk}^0 e_k^2$$

and

$$F_c = Ge_5Q + \sum_{i=1,3} \delta_i e_i Q^2 ,$$

with $A = a(T - T_0)$.

Using the principle of free-energy minimization and determining the corresponding second derivative, Errandonea obtained the temperature dependence of all parameters in this free energy. From Eqs. (7)–(9) and the free-energy expansion expressions in Eq. (11), the integral light scattering intensity of the soft optic mode is presented in the second column of Table I. The soft-mode frequency is also listed. The temperature variables noted here are $t = T - T_c$, $t' = T_c - T$, $g = 1/(T_c - T_0)$, and $g' = 1/(T'_0 - T_c)$ with $T_c - T_0 = G^2/aC^0_{55}$, $T'_0 - T_0 = (B'/2B)G^2/aC^0_{55}$), and

$$B' = B - 2 \sum_{i,j=1,3} (c^0_{ij})^{-1} \delta_i \delta_j .$$

An explicit fit to the experiment data requires a knowledge of the temperature parameters: g, g', T_c, and ratio $2B/B'$ in Eq. (11). Figure 1(b) illustrates the intensity versus temperature according to the formulas given in Table I with the temperature parameters obtained from frequency measurement. It is seen from the comparison of Fig. 1(b) with Fig. 1(a) that the bilinear optoacoustic coupling of eQ not only affects the optic soft mode's frequency behavior (it does not soften to zero) and shifts transition temperature but also changes the soft mode's intensity behavior.

In order to obtain the critical exponents, the alternative representations for intensity are given in the third column of Table I. The temperature variables are T_c, T_0, and T'_0. The critical exponents γ and γ' can be easily obtained from the I_1/T representation in double logarithmic scale, while β can be obtained from I_2/T with a given value of γ'.

III. EXPERIMENTAL RESULTS

Light scattering experiments were carried out in a normal 90° scattering geometry with an Ar^+ laser as excitation source. The oriented crystals of the two end's compounds in monoclinic I RP_5O_{14} LaP_5O_{14}, and TbP_5O_{14}, were used as samples. The temperature-control accuracy was ±1 °C. Figure 2 is the temperature dependence of

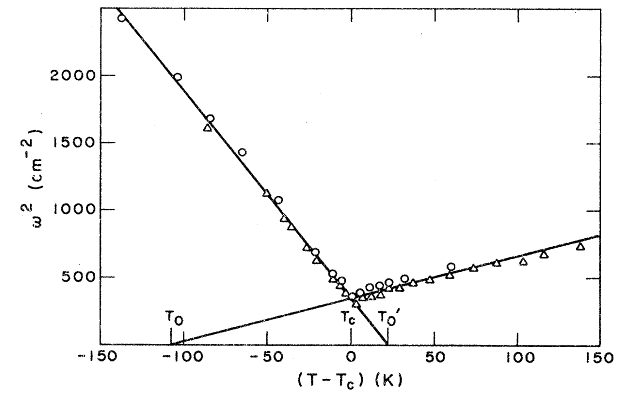

FIG. 2. A_g-$B_{2g}(ZX)$ soft-mode frequency square vs temperature in RP_5O_{14}. Both LaP_5O_{14} (△) and TbP_5O_{14}(○) data are included. The least-squares fit give the parameters: $2B/B' = -4.8$; $1/g = 109$ °C; $1/g' = 23$ °C.

the A_g-B_{2g} soft-mode frequency observed in $X(ZX)Y$ and $Z(XZ)Y$ geometries. The intersection of two $\omega^2 \sim T$ straight lines corresponding to temperature ranges above and below T_c determines T_c, which is found to be 122 °C for LaP_5O_{14} and 173 °C for TbP_5O_{14}. The intersections of these two high- and low-temperature branches with the temperature axis determine T_0 and T'_0, respectively. T_0 and T'_0 are found to be $T_c - T_0 = 1/g = 109$ °C and $T'_0 - T_c = 1/g' = 23$ °C; the ratio of the two slopes is $2B/B' = -4.8$. Figure 3 is the temperature dependence of the A_g soft-mode frequency observed in $X(ZZ)Y$ and $Z(YY)X$ geometries of LaP_5O_{14} and $Z(XX)Y$ of TbP_5O_{14}. The solid line is drawn identical to the low-temperature-branch solid line in Fig. 2.

The full width at half maximum (FWHM) of soft modes is in the range of ~7–10 cm^{-1} in the whole temperature region and the instrumental function is a Gaussian with a FWHM of 2.5 cm^{-1}. The integral soft-mode intensity is obtained after a deconvolution of instrumental function. It is apparent that the linear coupling mechanism is suitable for the case in which soft modes are Raman active both above and below T_c, while higher-order

TABLE I. Temperature dependences of the frequency and Raman-scattering intensities for the soft-optic mode under coupling forms of η to $\mathcal{E}$. C is intensity scale factor, descriptions of other parameters are given in the text.

Temperature region	$T < T_c$	$T > T_c$	$T < T_c$	$T > T_c$
Frequency $m\omega_Q^2$	$a\frac{2B}{B'}\left[t' + \frac{1}{g'}\right]$	$a\left[t + \frac{1}{g}\right]$	$a\frac{2B}{B'}(T'_0 - T)^{2\beta}$	$a(T - T_0)^{2\beta}$
Linear coupling intensity $\frac{I_1}{T}$	$C\frac{1}{a(2B/B')}\frac{1}{[t' + (1/g')]}$	$C\frac{1}{a}\frac{1}{[t + (1/g)]}$	$C\frac{1}{a(2B/B')}(T'_0 - T)^{-\gamma'}$	$C\frac{1}{a}(T - T_0)^{-\gamma}$
Quadratic coupling intensity $\frac{I_2}{T}$	$C\frac{1}{2B}\frac{t'}{t' + (1/g')}$	0	$C\frac{1}{2B}(T_c - T)^{2\beta}(T'_0 - T)^{-\gamma'}$	0
Cubic coupling intensity $\frac{I_3}{T}$	$C\frac{a}{2BB'}\frac{t'^2}{t' + (1/g')}$	0	$C\frac{a}{2BB'}(T_c - T)^{4\beta}(T'_0 - T)^{-\gamma'}$	0

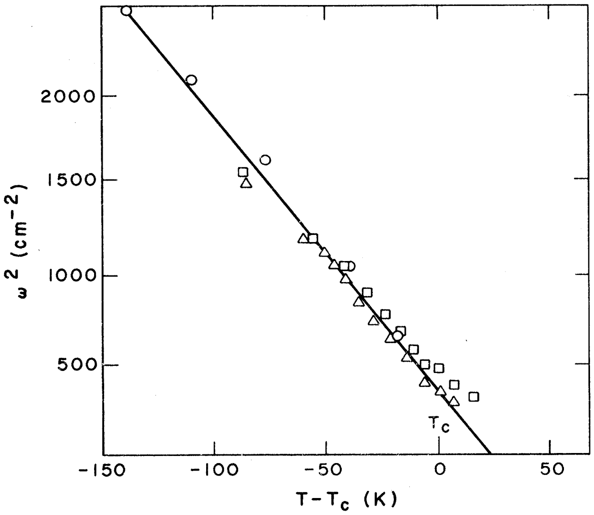

FIG. 3. $A_g(ZZ,YY,XX)$ soft-mode frequency square vs temperature in LaP_5O_{14}: $ZZ(\triangle)$, $YY(\square)$ and in TbP_5O_{14}: $XX(\bigcirc)$. The solid straight line is identical to the straight line of the low-temperature branch in Fig. 2.

couplings are appropriate for the soft modes (or polarizability components) which are Raman inactive above T_c. Figure 4 is the intensity for ZX spectra, corresponding to the A_g-B_{2g} soft mode for bilinear coupling of η to $\mathcal{E}$, I_1/T, in Table I. Figure 5 is the intensity fit for the ZZ,YY spectra of the A_g mode for the quadratic I_2/T expression in Table I. The fit parameters T_c, g, g', and $2B/B'$ are those obtained from frequency data. The dispersion of intensity data is mainly because of the instability of the experimental setup. We emphasize that the theoretical curves in Figs. 3 and 4 have *no* adjustable parameters, other than an overall vertical scale factor.

Figure 6 is a double logarithmic plot of ZX spectral intensity I/T versus $T_0'-T$ or $T-T_0$. The slopes of the

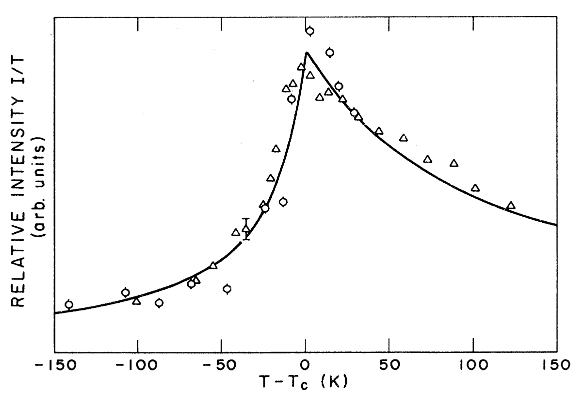

FIG. 4. ZX polarizability intensities in LaP_5O_{14} ($\square$) and TbP_5O_{14}($\bigcirc$). The solid curve is a fit to the theoretical I_1/T described in Table I for linear coupling of η to $\mathcal{E}$, with parameters given in the text and in the caption of Fig. 2.

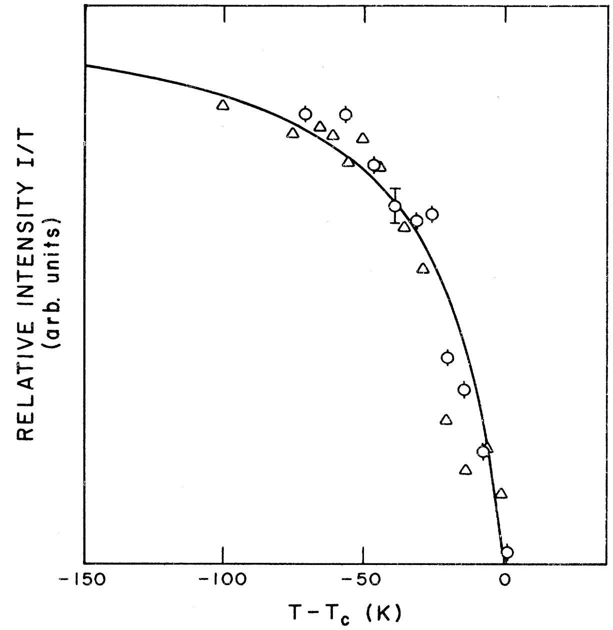

FIG. 5. ZZ ($\triangle$), YY ($\square$) polarizability intensities in LaP_5O_{14}. The solid curve is a fit to the theoretical I_2/T in Table I for quadratic coupling of η to $\mathcal{E}$, with parameters given in the text and in the caption of Fig. 2.

straight lines give $\gamma=1.16$ of LaP_5O_{14} for $T<T_c$, $\gamma=1.18$ of TbP_5O_{14} for $T<T_c$, and $\gamma=1.07$ of LaP_5O_{14} for $T>T_c$. Figure 7 is a plot of

$$\gamma'\ln(T_0'-T)+\ln(I/T)\sim\ln(T_c-T)$$

for ZZ and YY spectra of LaP_5O_{14}. The slopes give $\beta=0.47$ and 0.49, which are in good agreement with the β values of 0.46–0.50 according to frequency measurements.[4]

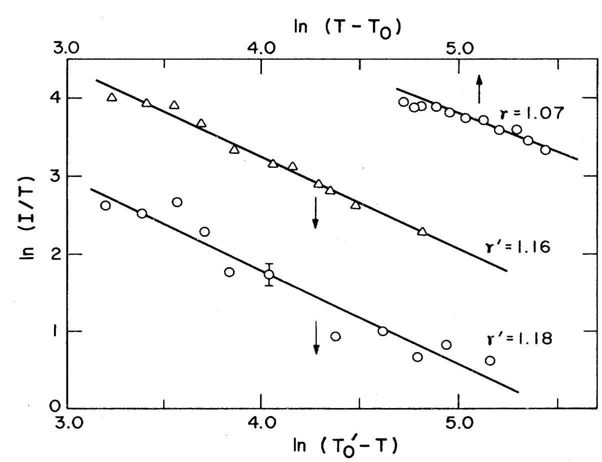

FIG. 6. Double logarithmic plot of ZX polarizability intensity of LaP_5O_{14} ($\triangle$), TbP_5O_{14} ($\bigcirc$) for $T<T_c$, and of LaP_5O_{14} ($\square$) for $T>T_c$.

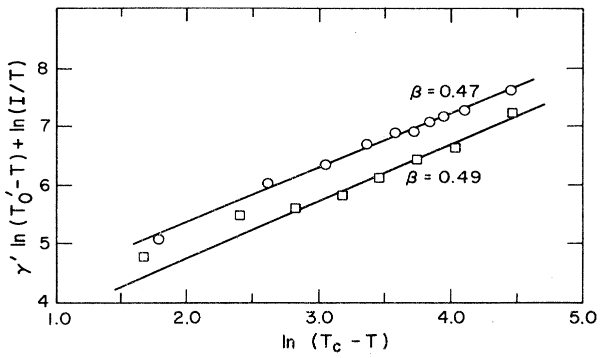

FIG. 7. Double logarithmic plot of ZZ (○) and YY (□) polarizability intensity of LaP_5O_{14}.

IV. DISCUSSION

We have found that a mean-field theory gives a good fit to our experimental data, utilizing a bilinear coupling form for the ZX polarizability intensities and quadratic coupling form for the ZZ, YY data. We have hoped that it would be possible to fit directly, as a single parameter, the quantity $(2\beta-\gamma)$ that appears as a temperature exponent for intensity in Fleury's theory. Such a direct measurement would be an extremely sensitive test of non-mean-field (fluctuation dominated) phenomena, since it provides a subtle test $(2\beta-\gamma\neq 0)$. However, when coupling is included, the intensity I_2 is given by

$$I_2/T=2B(T-T_c)^{2\beta}(T-T_0)^{-\gamma} \tag{12}$$

so that 2β and γ do not appear in the same exponent. This means that β and γ can be determined only as separate, correlated parameters in the least-squares fit.

The critical exponent α does not appear in these data analyses directly. Note, however, that through the Pippard relationship, the same value of α must describe the longitudinal-acoustic sound-wave velocity (LA ph) dependence near T_c and also the critical part of the specific-heat (SH) divergence near T_c.[11–14] More precisely, these two critical exponents are related as[15]

$$\alpha_{\rm SH}=\alpha_{\rm LA\,ph}-2(\phi-1)\ , \tag{13}$$

where the crossover exponent ϕ is 1.0 in the mean field, and $\alpha_{\rm heat}=\alpha_{\rm ph}$.

An expression of the Brillouin scattering intensity of the soft acoustic mode corresponding to c_{55} can be obtained under the same consideration for the soft optic mode. A comparison of theory and experiment is in progress.

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