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Magneto-structural coupling and harmonic lattice dynamics in $CaFe_2As_2$ probed by Mössbauer spectroscopy

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Abstract

In this paper we present a detailed Mössbauer spectroscopy study of the structural and magnetic properties of the undoped parent compound $CaFe_2As_2$ single crystal. By fitting the temperature dependence of the hyperfine magnetic field we show that the magneto-structural phase transition is clearly first order in nature and we also deduce the compressibility of our sample to be 1.67×10^{-2} GPa^{-1}. Within Landau's theory of phase transition, we further argue that the observed phase transition may stem from the strong magneto-structural coupling effect. The temperature dependence of the Lamb–Mössbauer factor shows that the paramagnetic phase and the antiferromagnetic phase exhibit similar lattice dynamics in high-frequency modes with very close Debye temperatures, $\Theta_D \sim 270$ K.

1. Introduction

The discovery of superconductivity (SC) with critical temperature (T_c) up to 55 K in iron–arsenide systems [1–3] has triggered enormous interest in iron-based superconducting materials. Generally, the parent compound undergoes a structural transition and exhibits antiferromagnetic (AFM) order below room temperature. Doping with electrons or holes into the parent compound will suppress the structural and magnetic transitions and induce SC [4]. Nowadays it is widely believed that SC is directly coupled to the magnetism in iron-based superconductors [5, 6]. There is also clear evidence about the strong spin–lattice coupling [7, 8]. Meanwhile, although the electron–phonon (e–p) coupling alone cannot explain the high critical temperature, it is proved that the e–p coupling effect definitely plays some role in the SC mechanism [9, 10], probably through the spin channel [11, 12]. Hence a better understanding of the magneto-structural coupling effect and the lattice dynamics in the iron–arsenide parent compounds is important in unraveling the SC pairing mechanism of the iron-based superconductors.

^{57}Fe Mössbauer spectroscopy (MS) is an excellent probe for both structural and magnetic local properties in iron-containing compounds. In iron-based superconductors the iron element serves as the primary constituent, which makes MS a useful analytical tool [13], especially for investigating the lattice dynamics in these systems. Indeed, MS has been widely used to study the iron-based superconductors, e.g. ReFeAsO (Re = rare earth elements) [14, 15], the AFe_2As_2 (A = Ba, Ca, Eu) system [16–18] and LiFeAs [19]. However, the properties regarding the magneto-structural coupling effect and the lattice dynamics are hardly discussed in most of these works. In the present work, single crystals of $CaFe_2As_2$ were synthesized and studied in detail by MS in the temperature range of 18–290 K. It was found that upon cooling through 170 K, $CaFe_2As_2$ undergoes a first-order magneto-structural phase transition and changes from a tetragonal $ThCr_2Si_2$-type paramagnetic (PM) phase to an orthorhombic AFM phase [20, 21]. Our observations suggest that the lattice dynamics of both the tetragonal and orthorhombic phases are very similar in the high-frequency modes, which could be denoted by the almost identical Debye temperatures of the two phases.

2. Experiments

Single crystals of $CaFe_2As_2$ were grown by the Fe–As self-flux method described elsewhere [20]. The resistivity

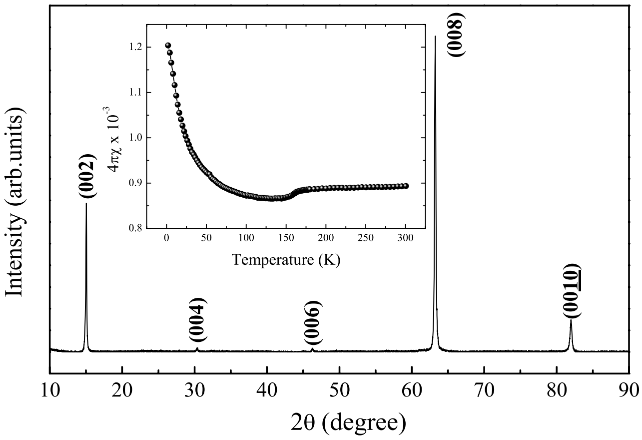

Figure 1. The single crystal x-ray diffraction pattern of $CaFe_2As_2$. The inset shows the temperature dependence of the magnetic susceptibility measured under $H = 5$ T.

and Hall effect analyses were reported earlier [20]. The phase purity of the crystalline sample was confirmed by single crystal x-ray diffraction measurements using a Philips X'Pert diffractometer with Cu Kα radiation. DC magnetization measurements were was carried out using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer. The transmission Mössbauer spectra were recorded using a conventional constant acceleration spectrometer with a γ-ray source of 25 mCi ^{57}Co in a palladium matrix moving at room temperature. The absorber was kept static in a temperature-controllable cryostat. All isomer shifts are quoted relative to α-Fe at room temperature. The Mössbauer spectra were fitted using the MOSSWINN 3.0I program [22].

3. Results and discussion

Figure 1 presents the single crystal x-ray diffraction pattern of the $CaFe_2As_2$ compound. The inset shows the temperature dependence of the magnetic susceptibility measured under $H = 5$ T. As can be seen, only (00l) diffraction peaks are observed, indicating that the crystallographic *c*-axis is perpendicular to the plane of the plate-like single crystal. The susceptibility curve shows an anomaly around 165 K corresponding to the magneto-structural phase transition, which is similar to previous reports [20]. All these results indicate that the sample has good quality and is hence a good starting point for the following MS measurements.

The ^{57}Fe Mössbauer spectra of the single crystal $CaFe_2As_2$ recorded in the temperature range of 18–290 K are shown in figure 2. Above 170 K, the spectra are quadrupole split paramagnetic lines and can be well fitted with only one asymmetric doublet. This means that the local environment of the Fe ion is unique, indicating that no impurity phases exist in the Mössbauer absorber. The spectra recorded at 160 and 165 K were fitted with a sextet corresponding to the AFM phase and an asymmetric doublet corresponding to the residual paramagnetic phase. The coexistence of both phases is characteristic for first-order phase transitions. At temperatures below 155 K, the spectra can be fitted with the superposition of two Zeeman patterns. Two subspectra are needed to obtain an improved fit to the observed spectra, which is similar to previous reports [23]. This may be understood as both commensurate (main component) and incommensurate (minor component) spin density waves (SDW) existing in the sample. The incommensurate SDW has also been observed in [23], where three sextets are used to fit the Mössbauer spectrum. Yet the incommensurability in 122-type iron-based parent compounds seems to be controversial. For example, for $BaFe_2As_2$ and $EuFe_2As_2$ compounds one component is enough to get a good fit to the spectrum and the shape of the SDW is quasi-rectangular [17] at low temperatures, while the shape of the SDW does not develop a fully quasi-rectangular shape [17] even at liquid helium temperature, which may be due to the incommensurate SDW. So, an understanding of the incommensurate SDW certainly deserves much more careful experimental examinations.

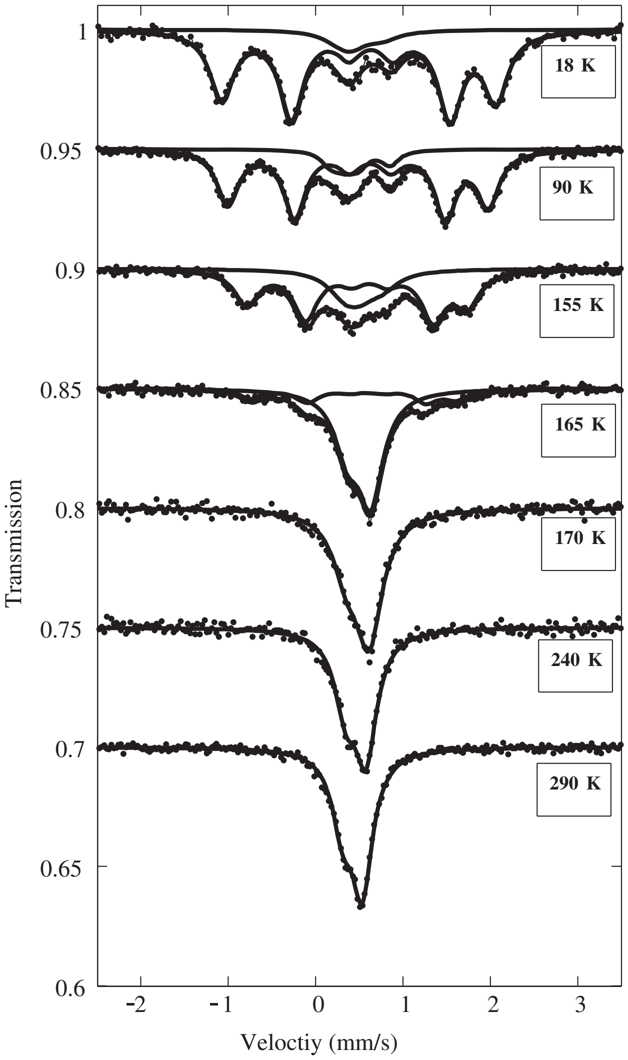

Figure 2. ^{57}Fe Mössbauer spectra of the single crystal $CaFe_2As_2$ obtained at the indicated temperatures. The spectra taken between 18 and 155 K were fitted with two Zeeman patterns as discussed in the text. The spectra recorded at 160 and 165 K were fitted with a sextet and an asymmetric doublet. The spectra taken above 170 K were fitted with only one asymmetric doublet.

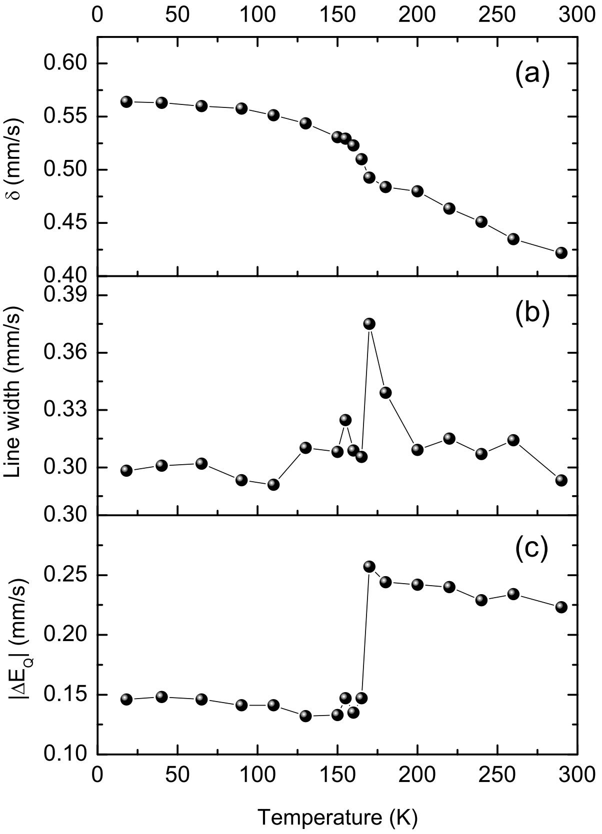

Figure 3. Temperature dependence of the Mössbauer hyperfine parameters extracted by fitting the spectra taken at different temperatures. (a) Isomer shift δ, (b) line width Γ, (c) quadrupole splitting $|\Delta E_Q|$.

The temperature dependences of the hyperfine parameters extracted by fitting the measured Mössbauer spectra at different temperatures are plotted in figure 3. It is well known that the total isomer shift (δ) is the sum of the chemical shift (δ_C) and the thermal shift (δ_{SOD}), i.e. $\delta = \delta_C + \delta_{SOD}$. As shown in figure 3(a), the isomer shift has a typical value of 0.42 mm s^{-1} for the 122-type iron-based superconductors at room temperature [13]. Upon cooling, δ increases gradually until 170 K, the characteristic of δ_{SOD}, then shows a sudden increase in a narrow temperature range, which could be mainly ascribed to the contribution of δ_C. In Mössbauer experiments, δ_C can be expressed as $\delta_C = \alpha(\rho_{\alpha Fe} - \rho_A)$ [24], where $\rho_{\alpha Fe}$ and ρ_A denote the electron density at the iron nucleus for α-Fe and the absorber, respectively. α is a calibration constant, which is positive for the ^{57}Fe nucleus. Thus, a positive isomer shift indicates a smaller electron density at the iron nucleus in the sample than in α-Fe. Therefore, the sharp increase in δ at ~165 K corresponds to a decrease in the electron density at the iron nucleus, which may arise from the changes of the unit volume at the transition temperature. The structural transition results in larger Fe–As distances in the orthorhombic phase, which reduces the interaction between Fe 3d and As 4p electrons and leads to more localized Fe 3d electrons. This will enhance the screening effect of the Fe 3d electrons to s electrons near the nucleus, causing smaller s-electron densities at the iron nucleus and thus a larger isomer shift.

The spectral line width, Γ, and quadrupole splitting, $|\Delta E_Q|$, are shown in figures 3(b) and (c), respectively. They both show an anomaly around 165 K, which is ascribed to the magneto-structural phase transition. One should notice that the line broadening actually appears at temperatures above the phase transition. A similar line broadening effect has been observed in $(Ba_{1-x}K_x)Fe_2As_2$ systems [16]. The most probable reason for the line broadening effect can be considered as the onset of magnetic order and/or short-range magnetic fluctuations that are present in the $CaFe_2As_2$ compound [8]. These observations highly suppose the magnetic origin of the magneto-structural phase transition in the $CaFe_2As_2$ parent compound. Upon cooling, some Fe spins happen to form clusters with short-ranged magnetic order in the nonmagnetic matrix by spin fluctuations of the Fe 3d charges. These spin clusters broaden the line width instead of the detectable hyperfine field. With further cooling, the phase transition occurs when the spin cluster reaches its critical point and causes structural distortion simultaneously to optimize the energy of the system due to the spin–lattice coupling effect. Therefore, it is suggested that the magnetic fluctuations and spin–lattice coupling effect may be responsible for the magneto-structural phase transition in the $CaFe_2As_2$ compound.

To examine the magnetic properties and obtain insight into the AFM phase transition, the temperature dependence of the hyperfine magnetic field is investigated using a mean field model after Bean and Rodbell [25], which, while describing the order parameter variation correctly, does not yield information about the magnetic fluctuations in the side of the hysteretic region, observed here. The reduced hyperfine magnetic field versus reduced temperature is plotted in figure 4 and the solid line is the calculated theoretical curve. In the Bean–Rodbell model, the temperature dependence of the sublattice magnetization in an AFM material is expressed as $T/T_0 = (\sigma/\tanh^{-1}\sigma)(1 + \eta\sigma^2/3)$ in the low spin state approximation [25]. $\eta = \frac{3}{2}Nk_B K T_0 \beta^2$, where σ is the reduced sublattice magnetization, η is a fitting parameter ($\eta < 1$ for a second-order transition, $\eta > 1$ for a first-order transition and for $\eta = 0$ the equation reduces to a Brillouin function), β is the slope of the dependence of the transition temperature on the volume, T_0 is the transition temperature if the lattice were not compressible, K is the compressibility, T is the temperature and k_B is the Boltzmann constant. As can be seen, figure 4 shows an approximate agreement between the theory and the experimental data. The observed hyperfine field decreases more rapidly with increasing temperature than the theory predicts in the low temperature range, which could be explained by the low-lying spin excitations as evidenced by the inelastic neutron scattering [8]. The fitted values of η and $B_{hf}(0)$ with fixed $T_0 = 170$ K are found to be 1.35 and 9.73 T, respectively. The value of η indicates that the nature of the AFM transition is of first order. This is in agreement with previously reported thermodynamic, transport and microscopic data [20]. The fitted zero point hyperfine field is very close to the value ($B_{hf} \sim 10$ T) reported by Kumar *et al* [23] at 4.2 K.

If we assume the Bean–Rodbell model to be valid, we may determine the compressibility of the $CaFe_2As_2$ compound.

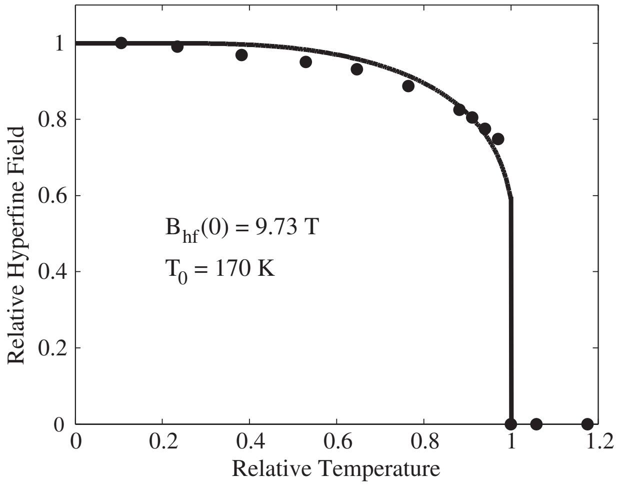

Figure 4. The reduced hyperfine magnetic field versus reduced temperature for the single crystal $CaFe_2As_2$ sample. The solid line is a theoretical fit to the experimental data obtained on heating, assuming $T_0 = 170$ K (see text).

According to the Bean–Rodbell model, the compressibility is given by $K = 6(\Delta v/v_0)^2/(\eta N k_B T_0 \sigma^4)$, where $\Delta v/v_0$ is the volume change at the transition. If we take experimental values, the volume change $\Delta v/v_0 = -0.93\%$ [26] (the negative sign of $\Delta v/v_0$ means a compression of the lattice during the AFM/PM transition, which is consistent with the Bethe–Slater curve), $T_0 = 170$ K, $\sigma = 0.77$ (taken at $T = 165$ K), $\eta = 1.35$ and, assuming $N = 2.79 \times 10^{28}$ m^{-3} (corresponding a density of 7 g cm^{-3}), we get $K = 1.67 \times 10^{-2}$ GPa^{-1}. This result is very close to the value from first principles calculations on $CaFe_2As_2$ ($K = 1.65 \times 10^{-2}$ GPa^{-1}) [27], while a little larger than the reported experimental values, 1.04×10^{-2} GPa^{-1} for the LaFePO [28] and 0.98×10^{-2} GPa^{-1} for the $Nd(O_{0.88}F_{0.12})FeAs$ [29]. Thus a direct measurement of the compressibility would be a useful check on this theory.

As discussed above, the magneto-structural phase transition in $CaFe_2As_2$ is first order in nature. In order to obtain a theoretical interpretation of our experiments, we adopt the phenomenological Landau theory of phase transitions to the system under study. In Landau's theory the free-energy density of the system is expanded in terms of two order parameters of σ (sublattice magnetization) and ε (strain) as [30]

$$F(\sigma, \varepsilon) = \tfrac{1}{2}a(T)\sigma^2 + \tfrac{1}{4}b\sigma^4 + \tfrac{1}{6}c\sigma^6 + \tfrac{1}{2}B\varepsilon^2 + \lambda\varepsilon\sigma^2, \quad (1)$$

where B is the elastic modulus and λ is the magneto-elastic coupling coefficient. Minimizing the total energy with respect to the strain yields $\varepsilon = -\lambda\sigma^2/B$. Substituting ε with σ in equation (1), one obtains a renormalized 2–4–6 Landau free energy,

$$F(\sigma) = \frac{1}{2}a(T)\sigma^2 + \left(\frac{1}{4}b - \frac{\lambda^2}{2B}\right)\sigma^4 + \frac{1}{6}c\sigma^6. \quad (2)$$

The magneto-elastic coupling is represented by the fourth-order term. To estimate the coefficient of this term, we turn to the Bean–Rodbell model, from which the magnetic part of the free energy without external field is also a 2–4–6 function of σ, as [31]

$$G(\sigma) = \tfrac{1}{2}(T - T_0)\sigma^2 + \tfrac{1}{12}(T - \eta T_0)\sigma^4 + \tfrac{1}{6}c\sigma^6. \quad (3)$$

Comparing equations (2) and (3), it is clear that the sign of $(b/4 - \lambda^2/2B)$ is determined by $(T - \eta T_0)$, which is negative when $\eta = 1.35$ around the transition temperature. A negative fourth-order term in the Landau free energy creates an energy barrier in the free-energy landscape; this leads to a first-order transition. Obviously, a large magneto-elastic coupling coefficient λ results in a large negative fourth-order term. The more negative this term is, the larger the transition barrier is, and the more distinct the first-order transition characteristics are. On the other hand, a larger λ leads to a larger spontaneous lattice distortion upon the magnetic transition. Therefore, the strength of the magneto-elastic coupling λ can be represented by the magnitude of the spontaneous lattice distortion, like η, which involves the parameters K and β that are related to the volume change. η also controls the order of the magnetic phase transition. According to equation (3), one always gets a negative fourth-order term when $\eta > 1$, indicating a first-order magnetic phase transition at T_0 due to the energy barrier from magneto-elastic coupling. Thus, the parameter η predicts the strength of the coupling.

To investigate the lattice dynamics of the Fe atoms, the temperature dependence of the Lamb–Mössbauer factor or recoil-free fraction, f, is discussed in what follows. In the Debye model of the lattice dynamics, f can be expressed as [24]

$$f(T) = \mathrm{e}^{\frac{-6E_R}{k_B\Theta_D}[\frac{1}{4}+(\frac{T}{\Theta_D})^2\int_0^{\Theta_D/T}\frac{x\,\mathrm{d}x}{(\mathrm{e}^x-1)}]}, \quad (4)$$

where k_B is Boltzmann's constant, Θ_D is the Debye temperature, and E_R is the recoil energy of an free emitting nucleus. In the high temperature ($T > \Theta_D/2$) approximation, we may rewrite equation (4) as the following formula [24]:

$$-\ln(f(T)) = \frac{6E_R T}{k_B\Theta_D^2}(1 + \epsilon T + \delta T^2 + \cdots). \quad (5)$$

Here ϵ and δ are termed as the anharmonic coefficients and they are both very small values.

The temperature dependence of $-\ln(f(T)/f(18\text{ K}))$ is shown in figure 5. It is evident that upon cooling the curve drops steeply through 170–150 K due to the occurrence of the phase transition. This sudden increase in $f(T)$ is likely to be due to the thickness effect, i.e. the increase of the spectral area when overlapping peaks separate from each other, as usually happens when a magnetic phase transition takes place [22]. The temperature dependence of $f(T)$ beyond this temperature region is quite linear, i.e. the Fe atoms experience harmonic vibrations in both the tetragonal phase and the orthorhombic phase. Since the anharmonic effect characterized by ϵ and δ is negligible, the $f(T)$ data can be simply fitted with $-\ln(f(T)/f(18\text{ K})) = 6E_R T/k_B\Theta_D^2 + \ln(f(18\text{ K}))$, where $\ln(f(18\text{ K}))$ is treated as a free parameter. The best fit of the experimental data shown in figure 5 yields the following results: $\Theta_D = 272$ K for the segment below the phase transition and $\Theta_D = 271$ K for the segment above

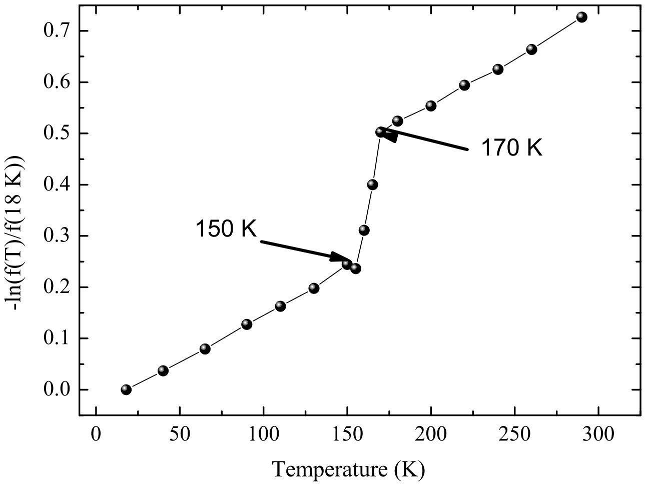

Figure 5. Logarithm of the relative f factor versus temperature.

the phase transition. The nearly identical behaviors of $f(T)$ with temperature indicate that there are no obvious changes of the phonon modes in the high-frequency ranges of the Fe vibrational state, which is in agreement with the inelastic neutron scattering results [32] on the phonon spectrum. Moreover, the observed harmonic vibrational behavior of the iron atoms indicates that the large phonon linewidths in $CaFe_2As_2$ observed by neutron scattering [33] may be due to the strong electron–phonon coupling effect. Furthermore, theoretical calculations of the phonon spectrum show that inclusion of the magnetism does not improve the agreement with experiments [33] for $CaFe_2As_2$. This is rather different from other 122-type, SrFeAsF [34] and LaFeAsO [35] 1111-type systems, where the authors show that inclusion of the magnetic degree of freedom greatly improves the agreement with experiments. Thus more work is necessary to understand these properties.

4. Concluding remarks

To conclude, we have studied the structural and magnetic properties of $CaFe_2As_2$ single crystal in detail by Mössbauer spectroscopy. Our results show that the structural distortion and magnetic transition are coalesced into one single first-order magneto-structural phase transition through the strong magneto-structural coupling effect. Short-range magnetic order and/or spin fluctuations appear well above the magneto-structural phase transition temperature and may be responsible for the phase transition. Analyzing the temperature dependence of the hyperfine magnetic field in the Bean–Rodbell model, we are able to determine the compressibility of the $CaFe_2As_2$ crystal, $K = 1.67 \times 10^{-2}$ GPa^{-1}. Both the PM and AFM phases exhibit similar lattice dynamic behaviors of the Fe atoms in high-frequency modes and they both have a Debye temperature close to ∼270 K.

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