

## Phonon Dispersion of bcc Iron to 10 GPa

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The phonon dispersion of bcc iron under high pressure to 10 GPa was measured at 300 K by inelastic neutron scattering. Its pressure dependence is surprisingly uniform. Contrary to the behavior found in other bcc elements, there is a lack of any significant pretransitional behavior close to the martensitic bcc-hcp transition which could be related to the Burgers mechanism. This finding confirms predictions by spin-polarized total energy calculations that explain the transition by the effect of pressure on the magnetism of iron. The high pressure frequencies were used to develop a lattice dynamical model from which thermodynamic quantities can be determined at any pressure to 10 GPa.

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There are currently intensive efforts to understand the phase diagram of iron and the transition mechanisms inherent to it [1–5]. At ambient conditions iron crystallizes in the bcc phase ( $\alpha$  iron) which transforms under pressure to hcp  $\epsilon$  iron at  $\sim 11$  GPa [1]. At pressures above  $\sim 50$  GPa and high temperatures the phase diagram is still controversial. Experimentally, several distorted hcp structures have been reported [1], the melting line is still not clearly defined [2], and first-principles calculations [3] are not conclusive, mainly because the presence of ferromagnetism complicates the problem considerably and reduces the predictive power of such techniques [2–5].

More generally, the behavior of bcc iron under compression is relevant since almost half of the elements contain the bcc structure in their phase diagram [6]. The lattice dynamics of bcc metals under variable temperature has attracted remarkable interest, the main issue being the search for dynamical precursor effects of lattice instabilities. Inelastic neutron scattering results exist for the alkali metals Li, Na, and K [7,8] at low temperature as well as for groups 3 and 4 transition metals like Zr, Ti, Hf, and Sc [9] at high temperatures. However, with the exception of a few data to 0.4 GPa on Na [8] and K [10], no lattice dynamical data are known under pressure. The behavior of the phonon dispersion of bcc metals under reduced volume is hence almost completely unknown, including the important case of iron.

In this Letter we report phonon dispersion data of Fe at room temperature up to 10 GPa, i.e., over almost the entire stability range of the  $\alpha$  phase. We compare these data with theoretical predictions of spin-polarized total energy calculations from which conclusions can be drawn on the bcc-hcp transition mechanism. We also present a lattice dynamical model which allows the description of the phonon dispersion over the entire Brillouin zone for any pressure between 0 and 10 GPa. This model, with the available data at high temperature and ambient pressure, should be able to describe fairly accurately the phonon dispersion of bcc iron in most of its  $P$ - $T$  domain. Our

measurements have been made possible by recent developments in high pressure and neutron instrumentation techniques [11]. The measurements were carried out using several single crystals of Fe (99.99% purity), 13–20 mm<sup>3</sup> in volume and of excellent quality (mosaic spread  $\sim 0.5^\circ$ ). The experimental setup was identical to previous experiments on Ge and Zn [11]. All measurements were carried out at the 2T1 triple axis spectrometer located at the ORPHEE reactor of the Laboratoire Léon Brillouin, Saclay, France. The pressure values were determined using the measured variation of the lattice parameter and the 300 K equation of state determined previously by x-ray diffraction measurements [12]. The mosaic spread of the single crystals used in the four different runs increased only slightly to  $\Delta \sim 0.7^\circ$  (FWHM) up to 11.3 GPa. In one run the pressure was increased to 12.0 GPa where  $\Delta$  increased to  $1.0^\circ$  indicating the onset to the  $\alpha$ - $\epsilon$  phase transition.

Most of the data were collected in the constant- $Q$  mode. Figure 1 shows spectra at ambient and high pressure of scans through transverse (TA) and longitudinal (LA) acoustical branches. The scans through the TA[100], LA[ $\frac{2}{3}\frac{2}{3}\frac{2}{3}$ ], and  $T_1$ [110] modes are among the most difficult ones with the lowest signal/background ratios due to their high energies. Nevertheless, the position of the phonon frequencies could be determined with a statistical error of  $< 1\%$  in almost all cases and the ambient pressure frequencies agree within  $\sim 2\%$  with those of Minkiewicz *et al.* [13] and De Vallera [15], as well as with earlier measurements by Brockhouse *et al.* [14] and Bergsma *et al.* [16].

Figure 2 shows the phonon dispersion along high symmetry directions containing 55 phonon groups at 0 and 9.8 GPa [17]. All measured frequencies increase by 5%–10% for a volume reduction corresponding to 5%. Of particular interest is the  $T_1$  mode with wave vector along [110] and  $[1\bar{1}0]$  polarization which is related at the zone center to the elastic constant  $C' = \frac{1}{2}(C_{11}-C_{12})$ . At the zone boundary ( $N$  point) it is seen to increase completely regularly, with a relative shift similar to the  $T_2$  mode with [100] polarization. This observation is important since

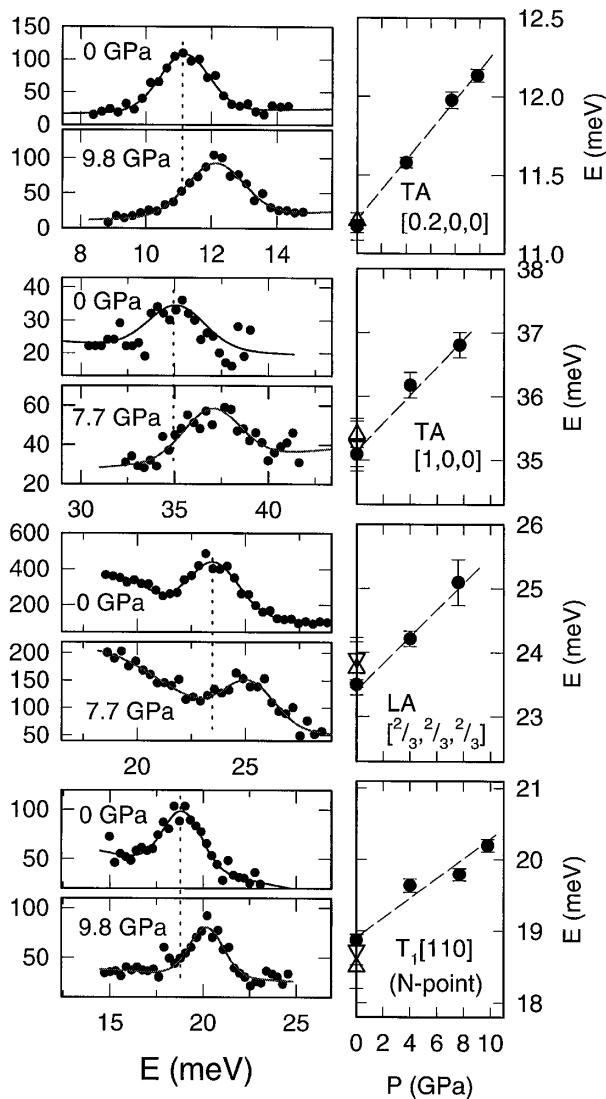


FIG. 1. Pressure dependence of four different phonon frequencies (figures on the right). The corresponding constant- $Q$  scans for ambient and maximal pressure are shown to the left. The solid lines represent least squares fits to a Gaussian including a linear background. Triangles indicate ambient pressure data of Refs. [13] ( $\nabla$ ) and [14] ( $\Delta$ ).

it concerns the transition to the high pressure  $\epsilon$  phase at  $\sim 10$  GPa. It was realized in 1934 by Burgers [18] that the hcp phase can be obtained from the bcc phase by (i) displacing adjacent (110) planes along [110] in opposite directions by  $\delta = a^{1/2}/12$  and (ii) shearing the lattice to change the octahedral angle from  $109.5^\circ$  to  $120^\circ$ . The displacement pattern for (i) corresponds precisely to the  $T_1(N)$  phonon [19] and it is expected that its frequency behaves anomalously close to the transition. In fact, *ab initio* calculations on Ba (where the bcc-hcp transition occurs at  $\sim 4$  GPa) predict a substantial softening of the  $T_1(N)$  phonon on approaching the transition pressure [20]. We find that in the case of iron such dynamical precursor effects due to the Burgers mechanism are definitely absent. The  $T_1(N)$  frequency shows no significant anomaly up to

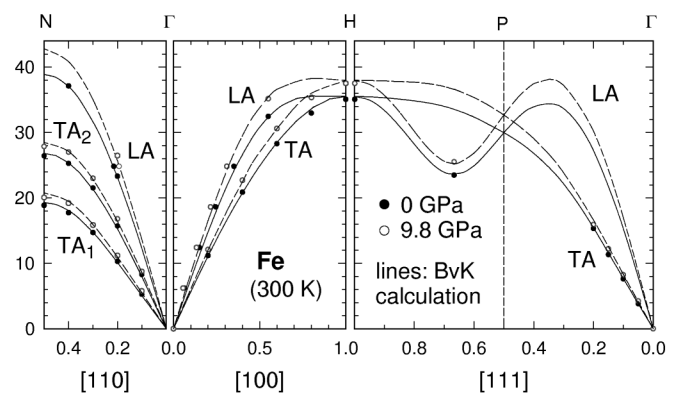


FIG. 2. Phonon dispersion of bcc iron at 0 GPa (full circles) and 9.8 GPa (open circles). The lines through the data points are fits using a Born-von Kármán model with interactions up to the fifth neighbor explained in the text. Vertical axis: energy in meV.

the transition pressure (Fig. 1), and this mode may have in fact a slightly larger positive Grüneisen parameter than the  $T_2(N)$  mode.

These results may be compared to predictions from spin-polarized full-potential total energy calculations by Ekman *et al.* [4]. Other published first-principles calculations (Ref. [5] and references therein) are not sufficiently specific on the volume dependence of phonon frequencies to be relevant for our study. The analysis of the  $T_1(N)$  mode [4] shows in fact a slight increase of its frequency in the 0–10 GPa range. The critical ingredient for this behavior is the presence of ferromagnetism which renders the bcc phase thermodynamically unstable long before it becomes dynamically unstable. At ambient pressure, the dominant role of magnetism for the stability of  $\alpha$  iron at ambient pressure is readily visible by an unusual feature of its phase diagram, the existence of a second, nonmagnetic, bcc phase ( $\delta$  iron) between 1660 K and the melting point at 1811 K. According to Ref. [4], the effect of pressure is essentially to broaden the flat  $d$  bands and thereby to decrease the density of states at the Fermi level  $D(E_F)$  below the stability limit for ferromagnetism given by the Stoner criterion  $I D(E_F) > 1$  ( $I$ : Stoner factor). The  $\alpha$ - $\epsilon$  instability is hence not primarily due to phonon softening but to the effect of pressure on the magnetism of iron, and our neutron data seem to confirm this.

The scenario of the bcc-hcp transition in iron is therefore different from the one which seems to exist in Ba under pressure [20]. It is certainly different from the situation found in group 4 transition elements Ti, Zr, and Hf where neutron studies at ambient pressure and elevated temperature have revealed a pronounced softening of the  $T_1(N)$  frequency as the hcp phase is approached [9,19]. Apart from these systems, the behavior of the lattice dynamics of other bcc elements close to a first-order martensitic transition to a hcp (or even fcc) phase is not known. It seems, however, that the bcc-hcp transition in iron is a rather exceptional case in the sense that no dynamical precursor

effects are visible on the  $T_1(N)$  mode. The presence of ferromagnetism in  $\alpha$  iron, a unique case among the bcc elements, is likely to be the reason for this.

To evaluate the phonon frequencies at any point of the Brillouin zone we performed lattice dynamical calculations on the basis of a general force constant (Born–von Kármán) model with interactions up to the fifth shell [23]. This model is identical to those applied in previous ambient pressure investigations on iron [13–16] and other bcc elements [24]. To take advantage of the bulk of published ambient pressure results [13–16] we used the data set of Minkiewicz *et al.* [13] and added to this the missing  $T_1$  branch from our own measurements (which is essentially identical to the one given by Brockhouse *et al.* [14]) to give a data set containing 80 phonons in total. This 0 GPa data set is the most detailed presently available on bcc iron at ambient conditions and gives force constants which deviate only insignificantly from those obtained in Ref. [13]. The calculated dispersion curves for this model are shown by the solid lines in Fig. 2. The force constants at 9.8 GPa were then obtained by adding the measured pressure-induced *shift* in frequency to the 0 GPa values given by the model. This procedure was applied since it eliminates calibration errors which are significant ( $\sim 1\%$ ) compared to the pressure-induced effects ( $\sim 10\%$ ). Only force constants up to the third shell were varied in the final refinements, with the remaining constants of the fourth and the fifth shell fixed at their ambient pressure values [25]. Varying only first-neighbor constants gave a very unsatisfying fit. It could be considerably improved by refining second-neighbor interaction ( $\alpha_2, \beta_2$ ) as well, but only to the expense of unrealistic values of  $\alpha_2$  and  $\beta_2$  as well as for the zone boundary frequency  $\omega_{LA}(N)$ . Relaxing third shell interactions ( $\alpha_3, \beta_3, \gamma_3$ ) gave an excellent fit with mean deviations of less than 0.17 meV, as shown by the dashed lines in Fig. 2 [26]. For this model it was also verified that the calculated phonon frequencies along zone-edge paths  $[\frac{1}{2}, \frac{1}{2}, \xi]$  and  $[\xi, \xi, 1]$  (not shown in Fig. 2) behave regularly. We therefore are confident that our model can accurately reproduce the phonon dispersion at 10 GPa for all wave vectors throughout the entire Brillouin zone.

This Born–von Kármán model allows one to calculate a number of elastic and thermodynamic parameters at 10 GPa to high accuracy. First, the elastic constants derived by the model (which takes into account the correlated data contained in the 55 phonons measured) are much bet-

ter defined (Table I) than those derived from shifts of individual mode frequencies as discussed above. The pressure coefficients  $\Delta C_{44}/\Delta P$  and  $\Delta C'/\Delta P$  of the two shear constants  $C_{44}$  and  $C' = \frac{1}{2}(C_{11}-C_{12})$  obtained for a pressure range of 10 GPa prove to be only slightly ( $\sim 5\%$ ) smaller than the ones determined by ultrasonic measurements to 1 GPa [27]. The variation of the elastic constants is thus remarkably linear over a large pressure range spanning almost the entire stability range of the bcc phase.

Next, the density of phonon states [frequency distribution function  $g(E)$ ] can be calculated by standard numerical integration which gives thermodynamic parameters such as the lattice specific heat at constant volume or the equivalent Debye temperature  $\theta_D$  (Fig. 3). As expected from Fig. 2, the trend of high pressure is to shift the spectral weight to higher energy, whereby the general form of  $g(E)$  remains remarkably similar. The Debye temperature at 0 K increases from 468 to 508 K and at ambient temperature from 421 to 457 K, a relative increase of 8.6% in both cases. This value is consistent with  $-\partial \ln \theta_D / \partial \ln V = 1.9$  derived from the pressure dependence of the elastic constants [28].

These results will enable one to determine the phonon dispersion of bcc iron over a large part of its stability range in the pressure-temperature domain. In fact, the temperature dependence at 0 GPa has been studied previously by different groups [15,21,22] and was fitted to exactly the same model as in this study. Assuming that the volume dependence of the phonon frequencies does not vary significantly with temperature, the phonon frequencies  $\omega(P, T)$  at any point in the  $(P, T)$  domain may be calculated or at least estimated to good precision. This can be done either by direct interpolation of the frequencies or by interpolation of the force constants [26]. The same applies to all thermodynamic parameters which can be extracted from the phonon density of states.

In conclusion, our data shed light on the bcc-hcp transition in iron. They present the first complete determination of the phonon dispersion of any bcc metal under high pressure. Although they are limited to 10 GPa and the  $\alpha$  phase, our results may be of considerable importance for the understanding of iron under extreme pressure and temperature, for two reasons. First, they provide highly detailed and accurate reference data for *ab initio* calculations which, at present, still give inconsistent results on iron at core conditions [3]. Second, they also provide benchmarks

TABLE I. Elastic constants of bcc iron at 300 K at 0 and 9.8 GPa. Values for this study were determined from a Born–von Kármán model fitted to the data as explained in the text. Previous ambient pressure neutron and ultrasonic data are given for comparison. Units are in GPa.

	$C_{11}$	$C = C_{44}$	$C' = \frac{1}{2}(C_{11}-C_{12})$
0 GPa: neutrons [15]	231.0	120.1	53.2
0 GPa: ultrasonic [27]	230.1	116.6	47.7
0 GPa: neutrons (this study)	223	122	48
9.8 GPa: neutrons (this study)	283	146	58

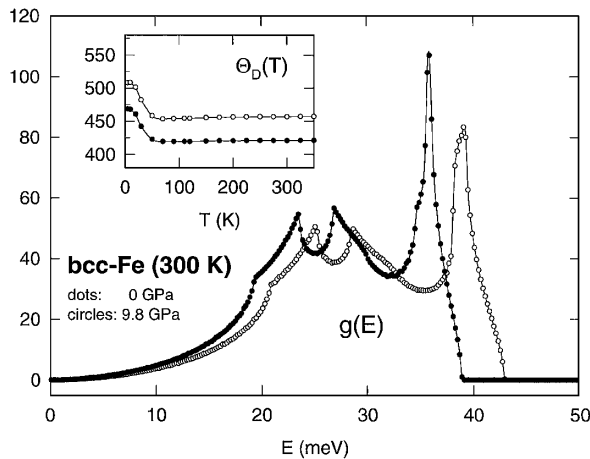


FIG. 3. Phonon density of states (frequency distribution function)  $g(E)$  at 300 K and Debye temperature  $\theta_D$  of bcc iron at 0 and 9.8 GPa.

for newly developed x-ray techniques which are able to derive, or at least estimate, elastic [29] and dynamical [30] properties of iron to much higher pressures. In both cases, our neutron data will set constraints and thereby contribute to a better understanding of iron under extreme conditions.

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