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The Elastic and Vibrational Properties of Cobalt to 120 GPa

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Impulsive stimulated light scattering and Raman spectroscopy measurements have been made on hcp cobalt to a static pressure of 120 GPa. This is the highest static pressure to date at which acoustic velocities have been directly measured. We find that at pressures above 60 GPa the shear elastic modulus and the Raman frequency of the E_{2g} transverse optical phonon exhibit a departure from a linear dependence on density. We relate this behavior to a collapse of the magnetic moment under pressure that has been predicted theoretically, but until now not observed experimentally.

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Under ambient conditions Co is known to be ferromagnetic and to exhibit either hcp (ϵ) or fcc (γ) symmetry. The latter phase is only metastable. A transition from the hcp to the fcc structure occurs at elevated temperature (695 K), and is followed by an isostructural transition to a paramagnetic phase with a Curie temperature, T_c , of 1400 K. The ϵ -Co phase is stable over a wide pressure range at room temperature, but it transforms to the fcc phase in the pressure range of 105-150 GPa [1]. There is no measurable change of volume at the transition, but thereafter the slope of the compression curve is reduced, indicating a net increase of the elastic stiffness. This fact was interpreted in Ref. [1] as an indication of the nonmagnetic nature of the high-pressure phase (β) in contrast to the ambient pressure magnetic γ phase. This is in accordance with the known collapse of the magnetic moment in transition metals and their compounds under high pressure [2]. Magnetization in 3d metals is related to a nearly complete filling of the majority 3d band, while the minority 3d band is only partially filled. It is the filling factor of the latter band, which determines the structure and elastic properties of these metals [3]. The effect of pressure is to widen the electronic bands, which in turn leads to a decrease of the density of states at the Fermi level, N_F , such that the stability condition, given by the Stoner equation ($N_F S > 1$, where S is the Stoner factor) for the magnetic state is no longer met.

Indeed, theoretical calculations [4,5] predict a suppression of the magnetism in the hcp lattice at a pressure of 180 GPa. Moreover, another theoretical calculation predicts that the fcc structure (nonmagnetic) is the more stable phase at 80 GPa [5]. The hcp phase of Co at ambient pressure is stabilized by the presence of magnetic moments, similar to

other magnetic 3d metals (e.g., bcc Fe) [3]. Thus, one can expect this phase to have anomalous elastic and vibrational properties. In fact, theory predicts anomalously soft elastic constants in 3d magnetic metals compared to their 4d and 5d counterparts [3]. The bulk modulus of hcp and fcc Co experimentally determined from the pressure-volume curves [1,6], and the elastic constants measured at ambient pressure, confirm this conjecture.

The magnetic 3d transition metals are excellent model systems to test the validity of current electronic structure calculations in the presence of magnetism. This is important for a wide range of scientific problems such as high-temperature superconductivity and colossal magnetoresistance. Application of pressure provides a convenient way for changing the physical properties of the system and driving it to a nonmagnetic state. Also, the study of magnetic 3d metals under pressure is important for a better understanding of the composition and structure of the Earth's interior. The behavior of Co is closely associated with the physical properties of another 3d magnetic metal, Fe, which is the major constituent of the Earth's core.

In spite of recent advances in diamond anvil cell techniques [7], accurate determination of the elastic and vibrational properties of metals under pressure of the order of 100 GPa, remains a challenging problem. In this letter we report the first measurements of the shear and compressional elastic constants by impulsive stimulated light scattering (ISLS) and also the frequency of the E_{2g} phonon by Raman scattering [8,9] of Co to 120 GPa. These two techniques ideally complement each other in determining the lattice dynamics

because they probe phonon branches at the center (ISLS), and at the boundary (Raman scattering) of the Brillouin zone (actually the extended Brillouin zone for Raman scattering). The results show that the pressure dependences of the elastic properties of hcp Co depart normal behavior long before the pressure range of the transition. There is a concomitant and abnormal decrease in the E_{2g} mode Gruneisen parameter, which suggests the approach of a lattice instability due to the collapse of the magnetic moment.

The application of ISLS to opaque materials in the diamond anvil cell has been described previously [10]. As in our work in hcp Fe [11], we determine the velocity of the interfacial wave that propagates at the interface between the diamond culet and the metal sample. The relevant probe spot diameter was approximately 30 μm . The Raman technique used in this work is described in detail in our previous publications (see [12] and references therein).

Polycrystalline Co samples (of 99.99 % purity) in the form of foil were loaded into a rhenium or inconel gasket and compressed between the diamond anvils. Several ISLS and Raman runs (4-5 each) to 40-55 GPa with flat diamonds showed consistent and reproducible results. For the highest-pressure measurements (up to 120 GPa), one of the two identical flat diamonds with a culet diameter of 500 and 200 μm for the ISLS and the Raman investigations, respectively was replaced by a beveled anvil of bevel angle 9 degrees. The corresponding central flats of the anvils were 100 μm and 50 μm , respectively. The pressure was determined by averaging the results of several ruby gauges distributed in the probed area. The pressure gradient across the probed sample

area (30 and 10 micrometer diameter for the ISLS and Raman experiment, respectively) did not exceed 8% of the nominal pressure. The corresponding gradients for the low-pressure experiments were substantially smaller. All the experiments were performed at room temperature.

Fig. 1a provides examples of experimental ISLS time-domain series and corresponding power spectra. The power spectra (Fig. 1b) show the interfacial wave and occasionally diamond bulk waves. The interfacial excitation was extremely short lived, a few ns at most, with the acoustic energy leaking rapidly into the surrounding bulk material. The small number of acoustic oscillations limits our frequency resolution to ± 1 percent. A Green's function formalism [13] was used to obtain orientationally averaged aggregate shear and compressional moduli from the interfacial wave velocity. Necessary inputs for this calculation were the elastic constants and density of diamond [14] and the bulk modulus and density of cobalt [1,6]. We quote the accuracy of determination of compressional and shear elastic constants as ± 2 % and ± 5 %, respectively based on analysis of possible combined experimental errors related to a not an ideal diffraction geometry (because of the diamond curvature) and an uncertainty in extrapolation of the elastic properties of diamond to ultrahigh pressure.

Representative Raman spectra of hcp Co under pressure are shown in Fig. 2. A band was observed over the experimental pressure range [15] that we associate with the Raman active mode, the E_{2g} phonon, as in the case of other hcp metals [8,9,12]. The Raman frequency shows a monotonic increase with pressure, and this behavior will be further

discussed below. By combining these data with the measured pressure dependence of the lattice constants [1,6], it is possible to obtain (under the assumptions of Refs. [8,9]) an independent estimation of a single-crystal shear modulus c_{44} .

Fig. 3 shows the compressional and shear elastic moduli of cobalt as a function of pressure. Extrapolations of the measured moduli of cobalt to ambient pressure are in reasonable agreement with those obtained from the known single-crystal elastic tensor [16,17]. The aggregate values were obtained using the Voigt-Reuss-Hill averaging scheme. The elastic anisotropy of Co is relatively small at ambient pressure (e.g., a 5 % difference in the shear constants). The differences between the random and textured averages are much smaller (see the discussion in Ref. [18]), and are believed to be within the experimental precision. The shear modulus inferred from our data also matches reasonably well that obtained from our Raman measurements (Fig. 3). The agreement is perfect at high pressures. The theoretically calculated elastic moduli [4] are somewhat larger than our experimental values, but the experimental and theoretical pressure dependences are qualitatively very similar.

Our experimental sound velocities (Fig. 4) exhibit a sublinear dependence on density, in contrast to the linear dependence that is given by Birch's law [19]. Moreover, the shear modulus essentially levels off at pressures approaching the phase transition. This is very different to the behavior of the sound velocity in Fe, which is essentially linear with volume [11,18]. To explain this effect, we consider the possibility of a magnetoelastic coupling between an acoustic phonon and spin wave branches [20,21]. An effect of the

coupling is that the dispersion curves effectively repel each other, or can even form avoided crossings, with the result that the speed of sound may be renormalized compared to the case of no coupling or a nonmagnetic material. Our calculations do show such a possibility even at ambient pressure if we assume a very low magnetic anisotropy (<0.1 meV), the value of which is not known precisely [22,23]. At high pressure we assume that the magnetic branch softens as the magnitude of the magnetic moment decreases [22,24], at which point its energy is comparable to the phonon energies. To explore the possibility of the softening of the acoustic velocity at high pressure on the basis of this theory, it is necessary to know the pressure dependence of the magnetoelastic coupling constants. Unfortunately, to the best of our knowledge, these have not been determined.

Alternatively, it can be supposed that the acoustic phonon branches show an anomalous pressure dependence that is a precursor of the martensitic hcp-fcc transition [25]. It is instructive at this point to recall that at ambient pressure the hexagonal elastic constant c_{44} does show an anomalous dip (27% reduction) in the close vicinity of the hcp-fcc transition (no other anomaly is reported), and no anomaly is observed in the fcc phase [26]. In contrast, our data exhibit a non-linear dependence long before the transition for both the shear and, to a lesser effect, the compressional wave. This seems to correlate favorably with the pressure dependence of the magnetic moment (inset to Fig. 4). The pressure dependence of the Raman frequency of Co also shows a considerable reduction in slope unlike the situation in Fe [8], where only a weakly sublinear dependence has been observed (Fig. 5). This difference can most clearly be seen when analyzing the volume dependence of the mode Grüneisen parameter at constant temperature γ (see inset

to Fig. 5), which shows a very rapid decrease in the case of Co, while it decreases only moderately in the case of Fe [8]. Thus, both the Raman and ISLS data indicate that the frequency of the entire Γ -A phonon branch exhibits a gradually decreasing slope near the phase transition pressure, P_c . This effect is more pronounced near the zone center, which can be easily deduced from Fig. 3. Also, the experimental and theoretical data show very good qualitative agreement (Figs 3,4) that supports the magnetic-nonmagnetic nature of the hcp-fcc pressure driven transition.

In summary, we have extended direct measurements of elastic constants of metals to the 100 GPa pressure range. The shear elastic constants determined by both ISLS and Raman scattering exhibit anomalous behavior near the hcp-fcc transition, in remarkable agreement with theory [4]. Unlike the martensitic transition at ambient pressure, this anomalous behavior is seen long before the transition, which is consistent with the loss of magnetic moments at P_c . From the topology of the phase diagram [1], one can suggest the existence of a quantum critical point (e.g., Ref. [27]) at 0 K and 100-150 GPa. We anticipate enormously enhanced spin fluctuations and possibly unconventional superconductivity in the vicinity of this point (c.f., Fe). Finally, we would like to point out that the pressure and volume dependences of the elastic constants of Fe and Co are essentially different in the limit of ultrahigh pressures, being regular in the case of Fe and anomalous for Co in the vicinity of the hcp-fcc transformation. Thus, care must be taken when treating the high-pressure elastic properties of Co as analogous to those of Fe in the hcp phase, a possibility that has recently been suggested [28].

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15. In the pressure range of 10-35 GPa, the E_{2g} mode experiences a substantial broadening. We believe that this phenomenon is not related to the main topic of this publication, so it will be discussed in a separate paper.
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29. A single-crystal c_{44} elastic modulus is inferred from our Raman measurements, whereas the ISLS data refer to a shear modulus averaged in the plane of propagation.

Figures.

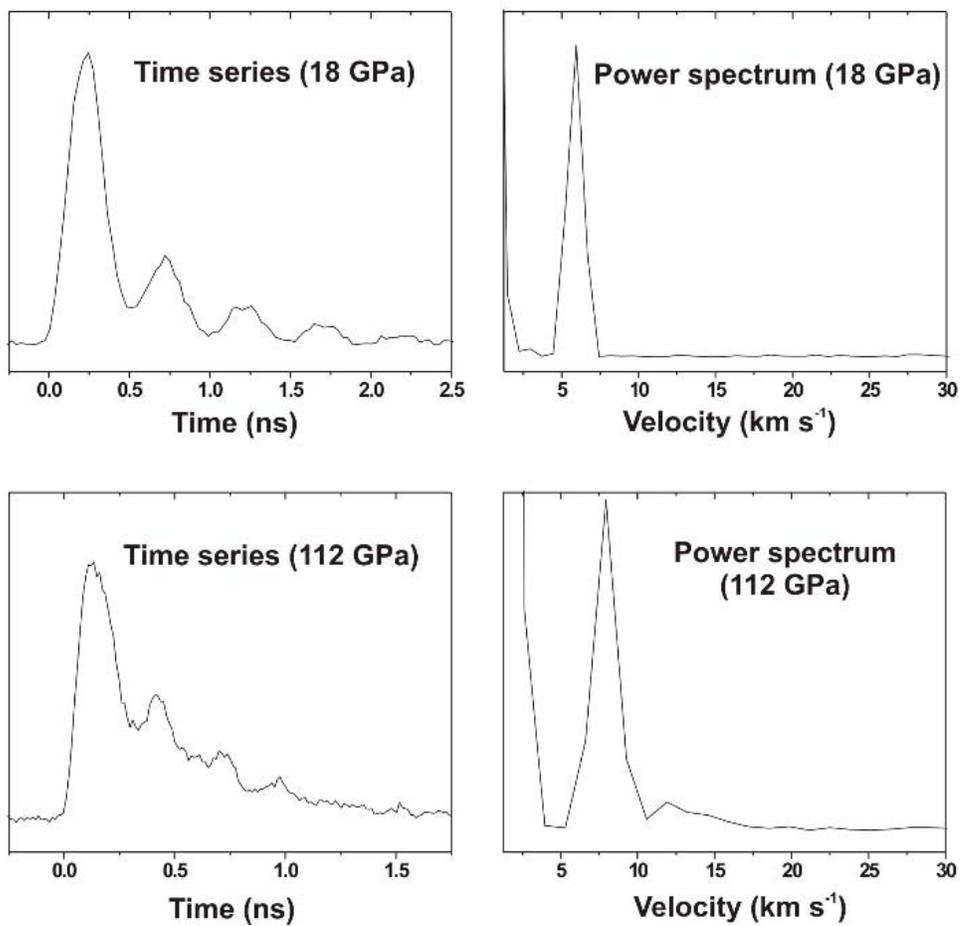


Fig. 1. ISLS time series obtained at 18 GPa (above) and 112 GPa (below). Acquisition time was approximately one minute. The corresponding power spectra are also displayed. The dashed lines represent the calculated line shape obtained using the Green's function formalism described in the text.

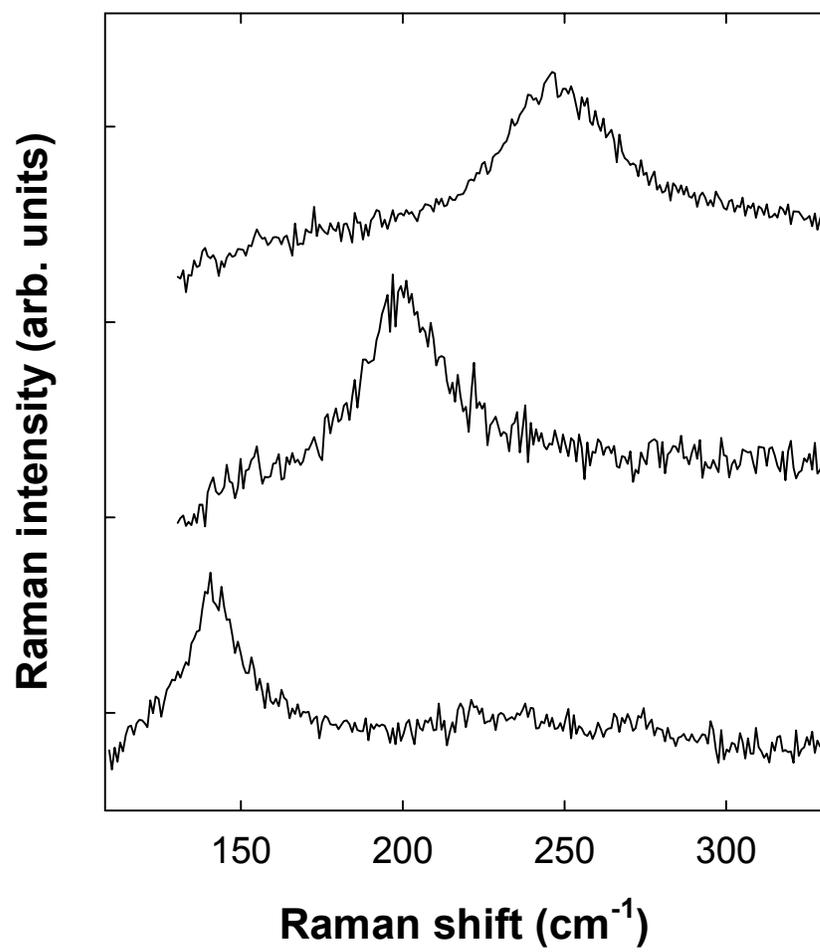


Fig. 2. Raman spectra of Co at elevated pressures.

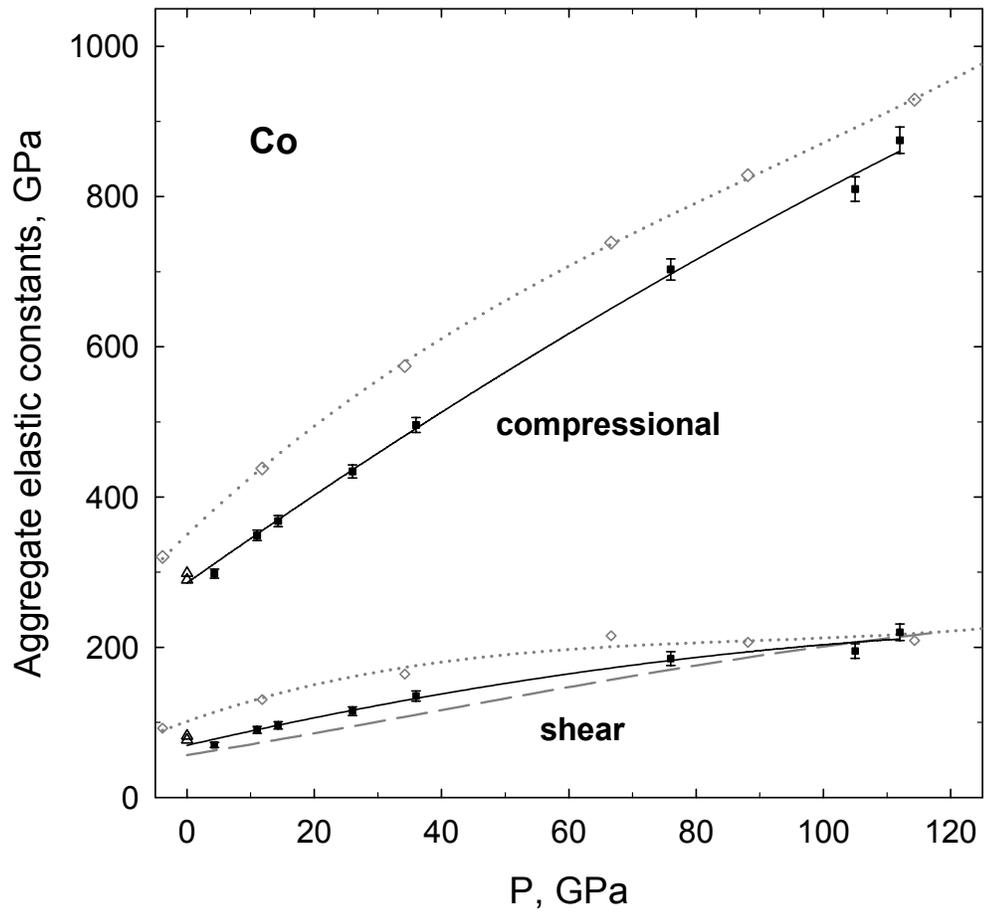


Fig. 3. Shear and compressional aggregate elastic constants of polycrystalline Co as a function of pressure. The full squares are our data. The solid lines are guides to the eye (second order polynomials). The experimental line is extrapolated to ambient pressure. The open triangles are ultrasonic literature data [16,17]. The open diamonds and dotted lines (a polynomial fit) are the results of theoretical calculations [4]. The dashed thick gray line is the value of c_{44} obtained from Raman measurements [29].

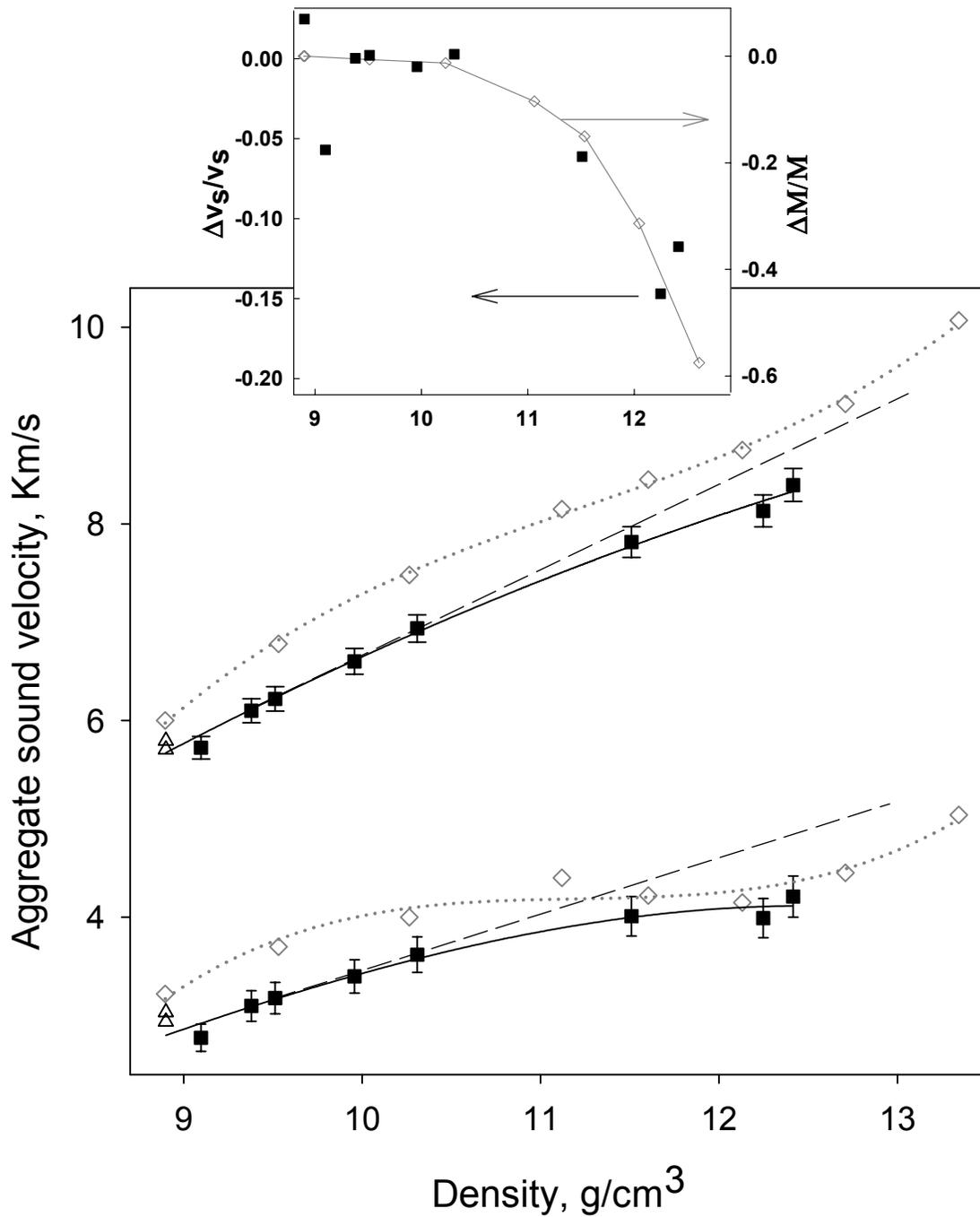


Fig. 4. Shear and compressional aggregate sound velocities of hcp-Co as a function of density. The full squares are our data, density is calculated according to Ref. [1]. Open triangles up- ultrasonic data [16-17]. The open diamonds and dotted lines (a polynomial

fit) are the results of theoretical calculations [4]. Long dashed lines represent linear extrapolation of the lower pressure data as one expects according to the Birch's law. The inset shows the density dependence of the magnetic moment relative change (gray line) after the theoretical calculations [4] and the relative deviation of the shear velocity from the linear dependence (squares).

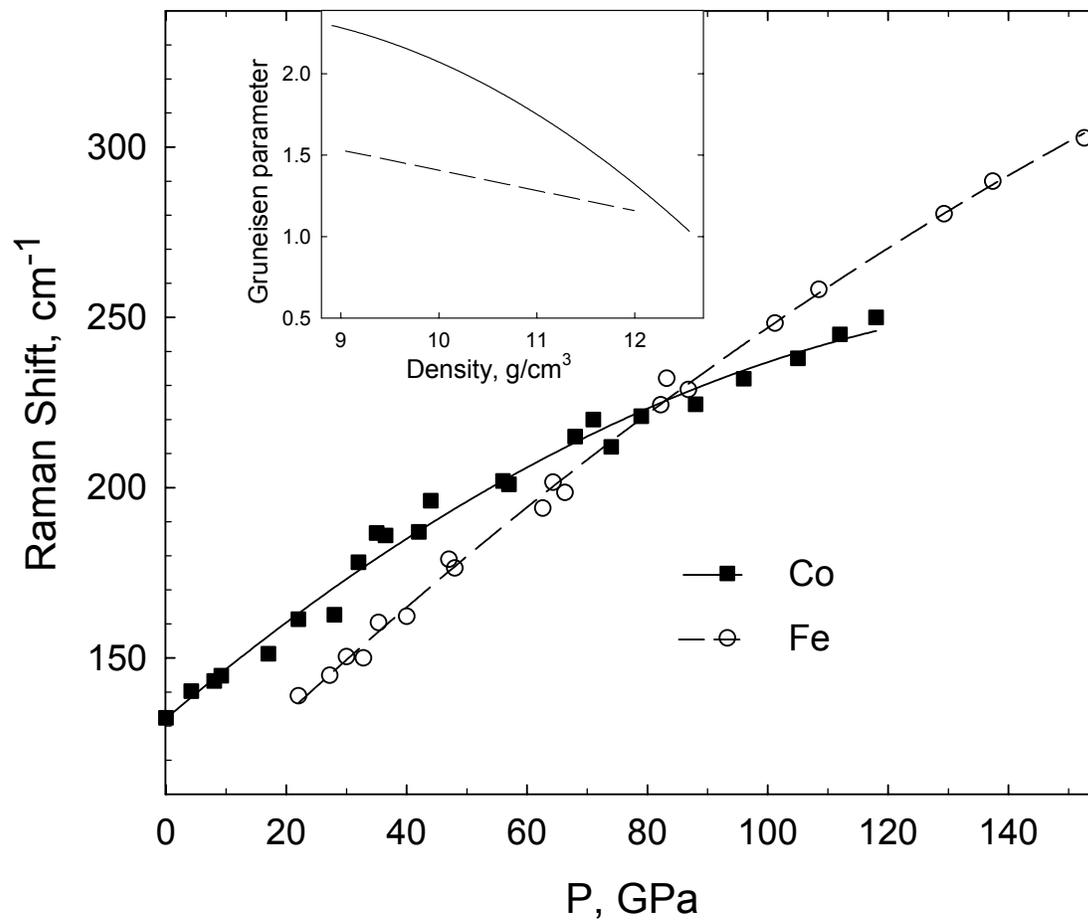


Fig. 5. Raman frequencies of Co (this work) and Fe [8] as a function of pressure. The inset shows the density dependence of the mode Grüneisen parameter, inferred from these data and pressure-volume curves [1,29].