Elastic and Vibrational Properties of Cobalt to 120 GPa

Alexander F. Goncharov, Jonathan Crowhurst, and Joseph M. Zaug
Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94551, USA
(Received 4 November 2003; published 17 March 2004)

Impulsive stimulated light scattering and Raman spectroscopy measurements have been made on hcp cobalt to a static pressure of 120 GPa. 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.

DOI: 10.1103/PhysRevLett.92.115502 PACS numbers: 62.50.+p, 62.30.+d, 63.20.Dj, 78.30.–j

Under ambient conditions Co is known to be ferromagnetic and to exhibit either hcp (ε) or—metastably—fcc (γ) symmetry. 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 3*d* metals is related to a nearly complete filling of the majority 3*d* band, while the minority 3*d* 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 3*d* metals (e.g., bcc Fe) [3]. One can thus expect this phase to have anomalous elastic and vibrational properties. Theory, for example, predicts anomalously soft elastic constants in 3*d* magnetic metals compared to their 4*d* and 5*d* 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 3*d* 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 3*d* 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 3*d* 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 from 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. 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. Other

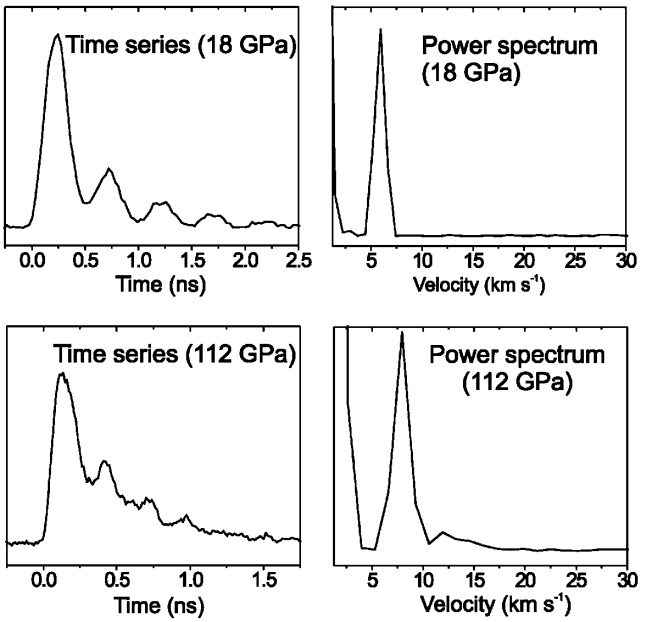

FIG. 1. ISLS time series obtained at 18 GPa (above) and 112 GPa (below). Acquisition time was approximately one minute. The corresponding power spectra are also displayed.

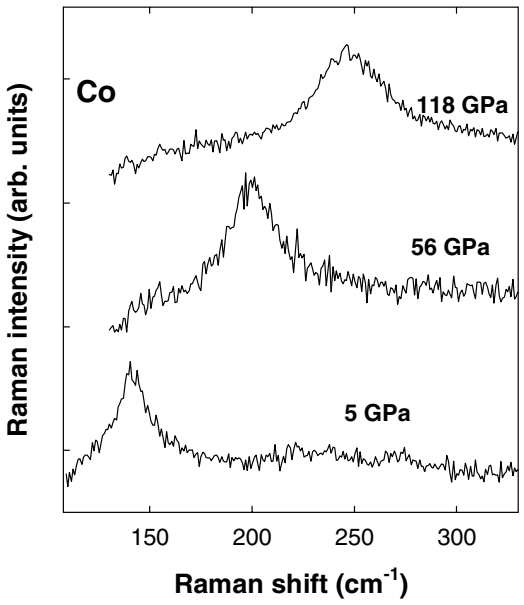

FIG. 2. Raman spectra of Co at elevated pressures.

experimental details are described in Ref. [11]. The relevant probe spot diameter for the present measurements was approximately 30 and 10 μm in ISLS and Raman measurements, respectfully. The Raman technique used in this work is described in detail in previous publications (see [12] and references therein).

Examples of experimental ISLS time-domain series and corresponding power spectra are displayed in Fig. 1. The power spectra show the interfacial wave and also 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]. The estimated uncertainties in the compressional and shear elastic constants were $\pm 2\%$ and $\pm 5\%$, respectively. These estimates were based on the measurement precision, but also took into account uncertainties due to diamond curvature, as well as those resulting from 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}.

Figure 3 shows the compressional and shear elastic moduli of cobalt as a function of pressure. Extrapolations of the measured moduli of cobalt to ambient

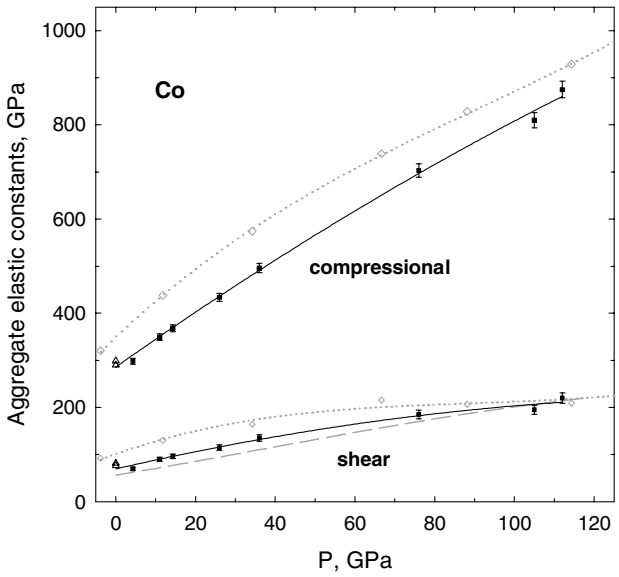

FIG. 3. Shear and compressional aggregate elastic constants of polycrystalline Co as a function of pressure. The full squares are our data. The solid lines are guides to the eye (second order polynomials). The experimental line is extrapolated to ambient pressure. The open triangles are ultrasonic literature data 16. 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 [16].

pressure are in reasonable agreement with those obtained from the known single-crystal elastic tensor [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 from

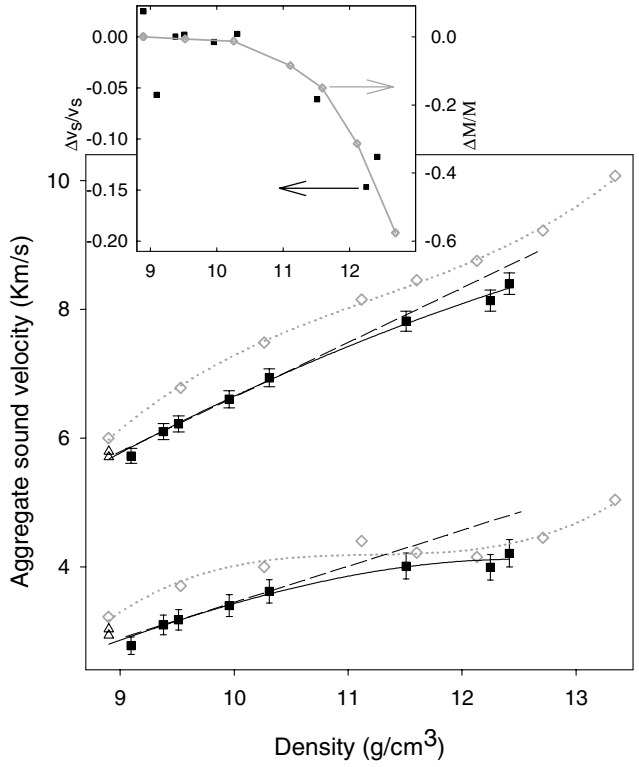

FIG. 4. Shear and compressional aggregate sound velocities of hcp-Co as a function of density. The full squares are our data, density is calculated according to Ref. [1]. Open triangles up- ultrasonic data [17]. The open diamonds and dotted lines (a polynomial fit) are the results of theoretical calculations [4]. Long dashed lines represent linear extrapolation of the lower pressure data as one expects according to 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).

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]. 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 [21,22]. At high pressure we assume that the magnetic branch softens as the magnitude of the magnetic moment decreases [21,23], 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 [24]. 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 [25]. In contrast, our data exhibit a nonlinear 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, but only a moderate decrease 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 and 4) that support 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,

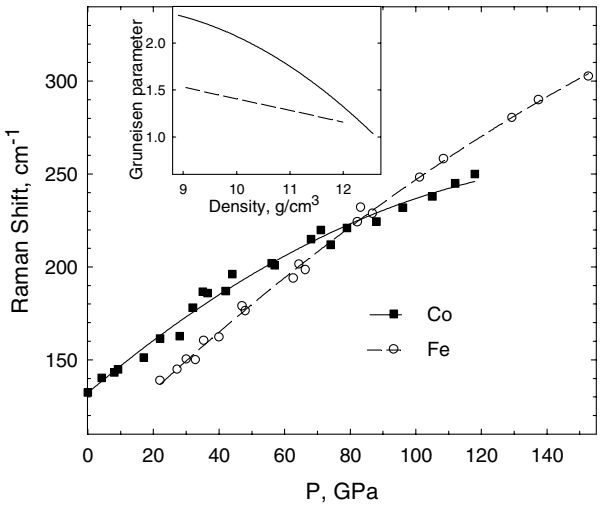

FIG. 5. Raman frequencies of Co (this work) and Fe [8] as a function of pressure. The inset shows the density dependence of the mode Grüneisen parameter, inferred from these data and pressure-volume curves [1].

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. [26]) 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 [27].

We thank G. Steinle-Neumann for providing us with the results of unpublished work and also V. Struzhkin and E. Gregoryanz for a critical reading of the manuscript. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

[1] C. S. Yoo, H. Cynn, P. Söderlind, and V. Iota, Phys. Rev. Lett. **84**, 4132 (2000).
[2] R. E. Cohen, S. Gramsch, G. Steinle-Neumann, and L. Stixrude, in *High Pressure Phenomena*, Proceedings of the International School of Physics "Enrico Fermi," Course CXLVII, edited by R. J. Hemley *et al.* (Società Italiana di Fisica, Bologna, Italy, 2002), p. 215.
[3] P. Söderlind *et al.*, Phys. Rev. B **50**, 5918 (1994).
[4] G. Steinle-Neumann, L. Stixrude, and R. E. Cohen, Phys. Rev. B **60**, 791 (1999); G. Steinle-Neumann (private communication).
[5] T. Jarlborg, cond-mat/0208424.
[6] H. Fujihisa and K. Takemura, Phys. Rev. B **54**, 5 (1996).
[7] R. J. Hemley and H. K. Mao, *Encyclopedia of Applied Physics*, edited by G. L. Trigg (VCH Publishers, New York, 1997), Vol. 18, p. 555.
[8] S. Merkel *et al.*, Science **288**, 1626 (2000).
[9] H. Olijnyk, A. P. Jephcoat, and K. Refson, Europhys. Lett. **53**, 504 (2001).
[10] J. C. Crowhurst *et al.*, Phys. Rev. B **64**, 100103 (2001); E. H. Abramson, J. M. Brown, and L. J. Slutsky, Annu. Rev. Phys. Chem. **50**, 279 (1999).
[11] J. C. Crowhurst, A. F. Goncharov, and J. M. Zaug (to be published).
[12] A. F. Goncharov and V. V. Struzhkin, J. Raman Spectrosc. **34**, 532 (2003).
[13] A. G. Every and G. A. D. Briggs, Phys. Rev. B **58**, 1601 (1998); A. G. Every, K. Y. Kim, and A. A. Mazenev, J. Acoust. Soc. Am. **102**, 1346 (1997).
[14] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **43**, 2944 (1972).
[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.
[16] 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.
[17] H. R. Schober and H. Dederichs, in *Elastic Piezoelectric Pyroelectric Piezooptic Electrooptic Constants and Nonlinear Dielectric Susceptibilities of Crystals*, edited by K.-H. Hellwege and A. W. Hellwege, Landolt Börnstedt, New Series III, Vol. 11a (Springer, Berlin, 1979); H. Masumoto, H. Saito, and M. Kikuchi, Sci. Rep. Res. Insts. Tohoku Univ. A **19** , 172 (1967).
[18] G. Fiquet, J. Badro, F. Guyot, H. Requardt, and M. Krisch, Science **291**, 468 (2001).
[19] F. Birch, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963), pp. 137–162; Geophys. J. R. Astron. Soc. **4**, 295 (1961).
[20] A. I. Akhiezer, V. G. Bar'iakhtar, and S. V. Peletminskii, Sov. Phys. JETP **36**, 157 (1959); G. A. Smolenskii *et al.*, *Physics of Magnetic Dielectrics*, edited by G. A. Smolenskii (Nauka, Leningrad, 1974).
[21] R. N. Sinclair and B. N. Brockhouse, Phys. Rev. **120**, 1638 (1960).
[22] X. Liu *et al.*, Phys. Rev. B **53**, 12 166 (1996).
[23] G. Shirane, V. J. Minkiewicz, and R. Nathans, J. Appl. Phys. **39**, 383 (1968).
[24] P. Tolédano *et al.*, Phys. Rev. B **64**, 144104 (2001).
[25] F. Frey *et al.*, Phys. Rev. D **9**, 603 (1979); B. Strauss *et al.*, Phys. Rev. B **54**, 6035 (1996).
[26] Debanand Sa, Phys. Rev. B **66**, 140505(R) (2002).
[27] D. Antonangeli *et al.*, Geophys. Res. Abs. **5**, 13826 (2003).