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Understanding Magnetic Exchange Interactions by the Pressure Dependent Curie Temperature in FeCoNiCuMn High Entropy Alloys

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Research Article

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This article is part of a special topical focus in the *Journal of Phase Equilibria and Diffusion* on the Thermodynamics and Kinetics of High-Entropy Alloys. This issue was organized by Dr. Michael Gao, National Energy Technology Laboratory; Dr. Ursula Kattner, NIST; Prof. Raymundo Arroyave, Texas A&M University; and the late Dr. John Morral, The Ohio State University.

Abstract:

We report the pressure (P) dependent Curie temperature, T_c (P) in a FeCoNiCuMn high entropy alloy (HEA). We analyze T_c(P) in terms of d-orbital contraction to explain changes in magnetic exchange interactions (J_{ex}). Considerations of the d-radius contraction inferred from the composition dependence of T_c in γ-Fe-Ni are combined with experimental data for P-dependent lattice constants and magnetic measurements of T_c(P), to calculate contributions of atomic spacing and d-orbital radii to J_{ex}. We show the d-orbital contraction with P captures most of the T_c variation in this alloy.

Introduction:

High entropy alloys (HEAs) are multicomponent systems where configurational entropy is larger than the fusion entropy of most common metals [1]–[4]. In many HEAs, BCC or FCC phases are entropically stabilized avoiding intermetallic formation to enhance solid solution strengthening [5]. The most frequently studied FCC HEAs are Cantor alloys consisting of equiatomic concentrations of Cr, Mn, Fe, Co, and Ni. [3] The magnetic behavior of the constituent atoms make then natural candidates for magnetic properties. HEAs have been studied for magnetocaloric effect applications primarily based on the hypothesis that the mixing of different atomic species would broaden the magnetic entropy curve and increase the working range of the material while retaining robust mechanical properties [6]–[10], though recent work by Law et al. has produced MCE HEAs with a first order magnetostructural transition as well [11]. Magnetic investigations of HEAs have optimized the magnetocaloric effect near room temperature and describe the discrete exchange interactions in the system which act to distribute contributions to the magnetic entropy [12]. Prior work on Cantor-like alloys containing Fe, Co, Ni, Cu and Mn has focused on the study of pairwise exchange bonds between magnetic atoms in the disordered magnetic systems and the dependence of Curie temperature, T_c, on composition and pressure.

Curie temperature engineering in metals with direct exchange interactions is based on understanding the T_c-dependence on interatomic distances and magnetic d-orbital overlap in predicting the magnetic exchange interactions, J_{ex}, by the Bethe-Slater curve. [13], [14] The Bethe-Slater curve was originally derived semi-empirically considering the Heitler-London theory of the chemical bond in the context of Heisenberg exchange [15], [16] and the constraints of the Pauli exclusion principle [17].

In the context of mean field theory [18], Heisenberg exchange interactions [15] are linearly related to T_c. While the Hartree-Fock equations are on firm theoretical footing, the solution of Schrödinger's equation with Slater determinantal wavefunctions become computationally intractable with increasing number of electrons. Hartree-Fock theory has been supplanted by considerations of a self-consistent field approximation [19] and the construction of an exchange correlation potential in local spin density functional theory (DFT) [20]–[22]. There are now many DFT calculations of exchange interactions in transition metal alloys [23].

Calculation of exchange interactions in the solid state are treated most correctly in solutions to relativistic Dirac equations [24]. Exchange integrals in the context of the Heitler-London theory [25] of the chemical bond were used to construct the Bethe-Slater curve [13], [14], [26], predicting the dependence of J_{ex} on D/d, where D is the transition metal interatomic spacing and d is the spatial extent of magnetic d-orbitals. In practice, exchange is more often discussed semi-empirically using Bethe-Slater curve predictions of 3d transition metal magnetic states. Since the Bethe-Slater curve is rooted in atomic bonding theory it may also be of future interest to view it in the context of universal binding energy ideas [27].

The Bethe-Slater curve is often used to highlight changes in exchange with changing atomic spacing, D, for example in Mn-Bi and alloys where increased Mn-Mn distance results in a switch from antiferromagnetic to ferromagnetic exchange [29]–[31] However, consider the change of T_c of the (FCC) disorder γ-Fe-Ni phase with composition (fig. 1b) [28], [32]. Since FCC Fe and Ni have very similar atomic size and lattice constants, the systematic change of T_c is not explained by atomic spacing, D, alone. Both FCC Ni and Fe fall directly on the Bethe-Slater curve (the latter on the left hand, negative antiferromagnetic region of the curve). Compositions in the binary alloys mimic the shape of the curve through the entirety of the range. We therefore consider a compositional dependence of J_{ex} arising chiefly from d-orbital contraction. The change in T_c for the Fe-Ni alloys depends on band filling causing d-orbital radius contraction with increasing Ni concentration. Thus, we consider atomic spacing, D, and d-orbital extent, d, as distinct variables to assess changes in J_{ex}. Given this evidence for the importance of d-orbital size on assessing change in magnetic exchange, we can assess the magnetic behavior of a system under applied pressure:

$$\begin{aligned}\frac{\partial J\left(\frac{D}{d}\right)}{\partial P} &= \frac{\partial J\left(\frac{D}{d}\right)}{\partial\left(\frac{D}{d}\right)}\frac{\partial\left(\frac{D}{d}\right)}{\partial P} \\ &= \frac{\partial J}{\partial\left(\frac{D}{d}\right)}\left(\frac{1}{d}\frac{\partial D}{\partial P} - \frac{D}{d^2}\frac{\partial d}{\partial P}\right) \\ &= \frac{\partial J}{\partial\left(\frac{D}{d}\right)}\left(\frac{1}{d}\frac{\partial D}{\partial P} - \frac{D}{d}\frac{\partial lnd}{\partial P}\right) \qquad (1)\end{aligned}$$

The $\frac{\partial J}{\partial\left(\frac{D}{d}\right)}$ term is from the slope of the Bethe-Slater curve itself. Note that because this leading term reflects the slope of the Bethe-Slater curve, it can be positive or negative depending on where on the curve we start. The term in parentheses can also be positive or negative depending on the relative importance of the pressure dependence of the lattice constant (interatomic spacing) or the extent of the d-orbitals.

Experimental Procedure:

FeCoNiCuMn HEAs were prepared by first arc melting elemental components multiples times to form a homogeneous ingot. Ingots were melt-spun to quench the alloys and retain a single, disordered FCC phase. Energy dispersive x-ray diffraction measurements were taken in a Paris-Edinburgh cell [33]–[35] at the HPCAT 16-BM-B high pressure station at Argonne National Lab's Advanced Photon Source. They were converted to conventional angle-dispersive spectra using Bragg's law. Spectra were taken for several applied pressures up to 6.77GPa. Magnetic measurements were performed in an M-cell 10 pressure cell fit into a Quantum Design SQUID magnetometer. Each sample was zero field cooled before a heating and cooling magnetization curve were taken at each applied pressure up to 750 MPa. Pressure was determined from the superconducting transition for a Sn manometer.

Results and Discussion:

To infer the change in the d_{3d} orbital diameter with applied pressure, we first consider experimental data accounting for the remaining terms of equation 1. The term $\frac{\partial J}{\partial\left(\frac{D}{d}\right)}$ is taken from the slope of the Bethe Slater curve, which we can parameterize based on expectation values of the diameter of the d-orbitals. D and $\frac{\partial D}{\partial P}$ can be obtained from the high-pressure x-ray diffraction (XRD) data (fig. 2a) of FeCoNiCuMn. Peaks were indexed to an FCC structure with an ambient pressure lattice constant of 3.61 Å. Fig. 2b illustrates the linear pressure dependence of the lattice spacing, a_{fcc}, and corresponding atomic spacing, D: $\frac{afcc}{\sqrt{2}}$. The $\frac{\partial D}{\partial P}$ term in equation 1 is thus -0.58 pm/GPa. The data of fig. 2a allows us to calculate the bulk modulus of the alloy, K=175 GPa. This value is comparable to steels, FCC late transition metals and is considerably larger than softer FCC Mn and Cu; it is also 10% higher than the average bulk modulus of all the elements making up the alloy. This is consistent with the “cocktail effect” noted in the mechanical properties of other HEAs [1], [2], [36], [37]. This indicates that excellent mechanical properties can be maintained in alloys with sizeable concentrations of elements (Mn, Cu) chosen for their effects in engineering the Curie temperature.

Fig. 3a illustrates the magnetization, M(T), curves for the $FeCoNiCu_{0.95}Mn_{1.05}$ (19 at% Cu, 21 at% Mn) alloy composition described in Kurniawan et al [7]. The data shows T_c for this alloy decreases with increasing applied pressure. T_c was estimated from inflection points on the M(T) curves, and calculated more precisely using an Arrott-Noakes equation of state [38] to ensure an accurate value of the derivative, $\frac{\partial T_c}{\partial \mathrm{P}}$, which is equal to -40.8 K/GPa. From the change in T_c with pressure (fig. 3b) we can estimate the value of $\frac{\partial \mathrm{J}\left(\frac{\mathrm{D}}{d}\right)}{\partial P}$ using mean field theory:

$$J_{ex} = \frac{3k_bT_c}{2S(S+1)}$$

The mean field value of the spin angular momentum, S, for these alloys was estimated to be S=1.5 based on an average of seven 3d electrons/atom, and comparison with similar alloys and their location on the Slater-Pauling curve. However, it should be noted that the fits are not sensitive to variation of S and thus the exact value used is not significant, as different S values will replicate the same compositional trends where the calculated values are simply scaled upwards. The calculations assume localized d-electrons, but unlike f-electron systems [39, Ch. 4], direct exchange is assumed with orbital angular momentum quenched by cubic crystal fields [32, Ch. 19]. This is consistent with evidence for discrete local pairwise exchange interactions observed in the hyperfine field distributions by Mössbauer spectroscopy [6]. The FCC structures of these alloys also leads to more localized moments than for BCC structures due to the strong ferromagnetism accompanying a Fermi energy lying in the minority spin d-bands [32, Ch. 19]. We therefore treat the electrons in these alloys as localized and presume that the chief contribution to the direct exchange interactions is from nearest neighbors. This can be contrasted with BCC FeCo for example where consideration of several nearest neighbor shells is required to capture the exchange [23].This experimental data gives us a change in J which can be mapped to the term $\frac{\partial J}{\partial\left(\frac{D}{d}\right)}$ in equation 1; combined with the data in fig. 2 which provides the term $\frac{\partial D}{\partial P}$, we thus have enough data to numerically calculate the $\frac{\partial lnd}{\partial P}$ term in equation 1 and calculate the average d-orbital size of the FeCoNiCuMn HEA as a function of P (fig. 4a). The calculations assume the alloy to lie on the righthand side of the Bethe-Slater curve based on its electrons to atom ratio and approximate d-orbital size at P=0, which are close to solid state values calculated by Slater and Mann [14], [40].

Our results clearly show the d-orbital contraction, along with d-band filling, and nuclear screening, are important to understanding J_{ex} in alloys. While the Bethe Slater curve is often used to describe the variation of J_{ex} with large atomic spacing variations [29], [30] d-orbital contraction must be considered to precisely account for its variation in disordered alloys with similar interatomic spacings. This is an important consideration in our analysis of T_c (P). Considering changes in atomic spacing (D) alone, we would expect T_c to increase with P in the FeCoNiCuMn HEA given that T_c (P=0) places it just beyond Ni on the Bethe Slater curve, and decreasing D independent of d would move the point to the left. However, we experimentally observe a decrease in T_c (movement to the right), which we explain by a small decrease in the d-orbital size (a 3.5% decrease at P=1GPa). Because the d-orbital decreases in size more rapidly than the atomic spacing, the $\frac{D}{d}$ ratio increases (fig. 4b).

The relative importance of d-orbital contraction on J_{ex} is evaluated considering the first and second terms in equation 1 separately. The differential in the first term accounts for the change in atomic spacing (D), while the second term depends on the change in d-orbital spatial extent. A direct comparison of the size of each term (fig. 4c) shows that, particularly at low pressures, the change in d-orbital radius dominates the overall change in exchange $J_{ex.}$ If we directly compare the change in D and d, $(^{\partial D}/_{\partial P})$ vs $(^{\partial d}/_{\partial P})$ (fig. 4d), the derivative terms intersect at 7GPa, after which the $\frac{\partial D}{\partial P}$ derivative becomes the larger of the two. However, the non-derivative multipliers for each term scale the influence of each such that the $\left(\frac{\partial d}{\partial P}\right)$ term always contributes more significantly to changes in $J_{ex.}$ Therefore, it would require enormous, applied pressures to cause a change in sign in J_{ex}. Thus, the inclusion of d-orbital contraction is essential to understand variations in J_{ex} in these HEAs. The initial contraction is postulated to be so large due to the compressibility of the free electrons allowed by their increased density in the FCC interstices of the alloy. This charge redistribution decreases the amount of d-orbital screening between atoms. However, Coulomb repulsion between s and d electrons eventually impedes this compression as orbitals necessarily push closer to the nucleus of neighboring atoms. The crossover at higher applied pressures may provide the driving force for their rotation in a structural or magnetic phase transformation.

There are limits to the conclusions we can draw from these results, primarily due to the distribution of magnetic exchange resulting from the sum of discrete interactions among various magnetic atoms. Mean field theory can only provide an estimate of the exchange energy for this system based on averages. The breadth of the magnetic transitions reflects the fluctuations in exchange interactions about this average and is a function of the d-orbital extent, also averaged over several atomic species. Additionally, d-orbital behavior is quite complex, and this work alone only contributes experimental grounding and guidance to the larger body of theoretical and computational analysis of d-orbital extent. Nevertheless, this analysis clearly illustrates the relative significance of d-orbital contraction as compared with traditional analysis of interatomic spacings alone in determining J_{ex}.

Conclusion:

We combine M(T) under pressure data, pressure-varied crystallographic data, and inferences about d-orbital behavior from the disordered γ-phase Fe-Ni T_c to demonstrate the importance of considering atomic spacing and d-orbital radii as separate variables when discussing changes in magnetic exchange energy under pressure. We show that the pressure dependent T_c for a FeCoNiCuMn HEA can be understood to be primarily due to the contraction of d-orbitals.

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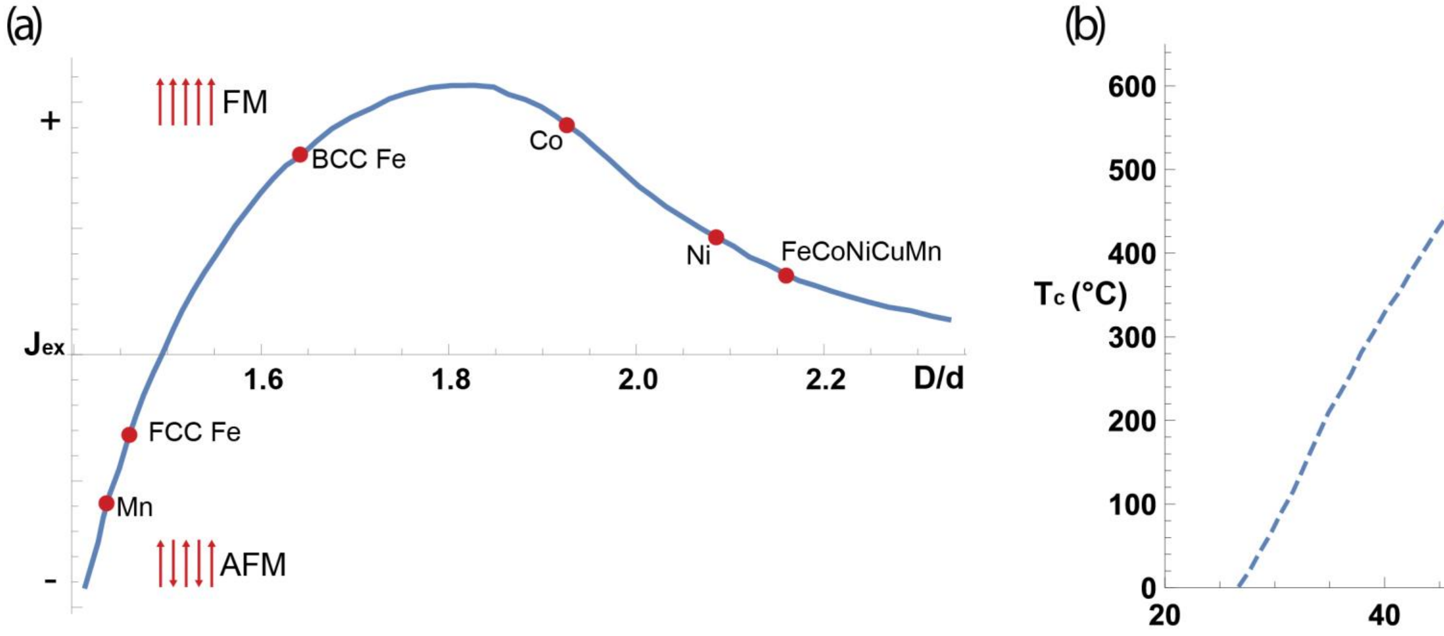
Figures:

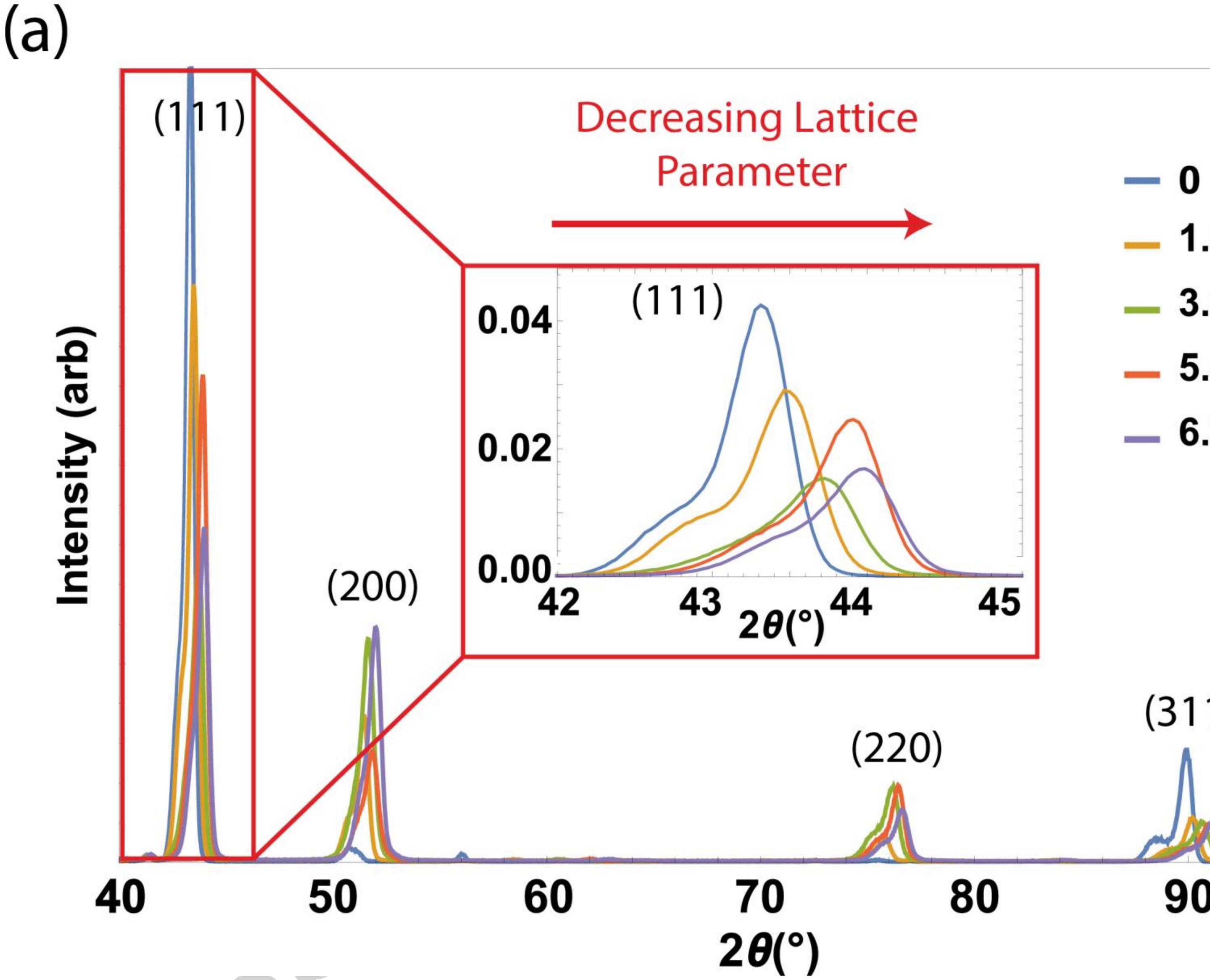
Fig. 1 (a) Bethe Slater Curve, showing the empirical relationship between J_{ex} and D/d_{3d}. Starting position of FeCoNiCuMn is based on value of T_c and estimated d-orbital size. (b) T_c of the disordered FCC Fe-Ni phase from 20% to 100% Ni, adapted from Swartzendruber [28]. ***Printed with permissions.**

Fig. 2 (a)XRD of FeCoNiCuMn as a function of applied pressure (b) linear relationship between lattice spacing (a) and pressure, with the calculated change in atomic spacing ($D=\frac{afcc}{\sqrt{2}}$).

Fig. 3 (a) Curie temperature determined from $\frac{dM}{dT}$ for a series of pressures. The inset shows the M(T) data. (b) The linear T_c vs P relationship plotted directly.

Fig. 4 (a) d orbital diameter versus applied pressure for the $FeCoNiCu_{0.95}Mn_{1.05}$ alloy. (b) $\frac{D}{d}$ ratio with applied pressure, which increases despite both D and d decreasing with pressure. (c) Magnitude of first term and second term from parentheses in equation 1. (d) Magnitude of $\frac{\partial D}{\partial P}$ vs $\frac{\partial d}{\partial P}$, showing that the change in D becomes greater than the change in d_{3d} around 7 GPa.

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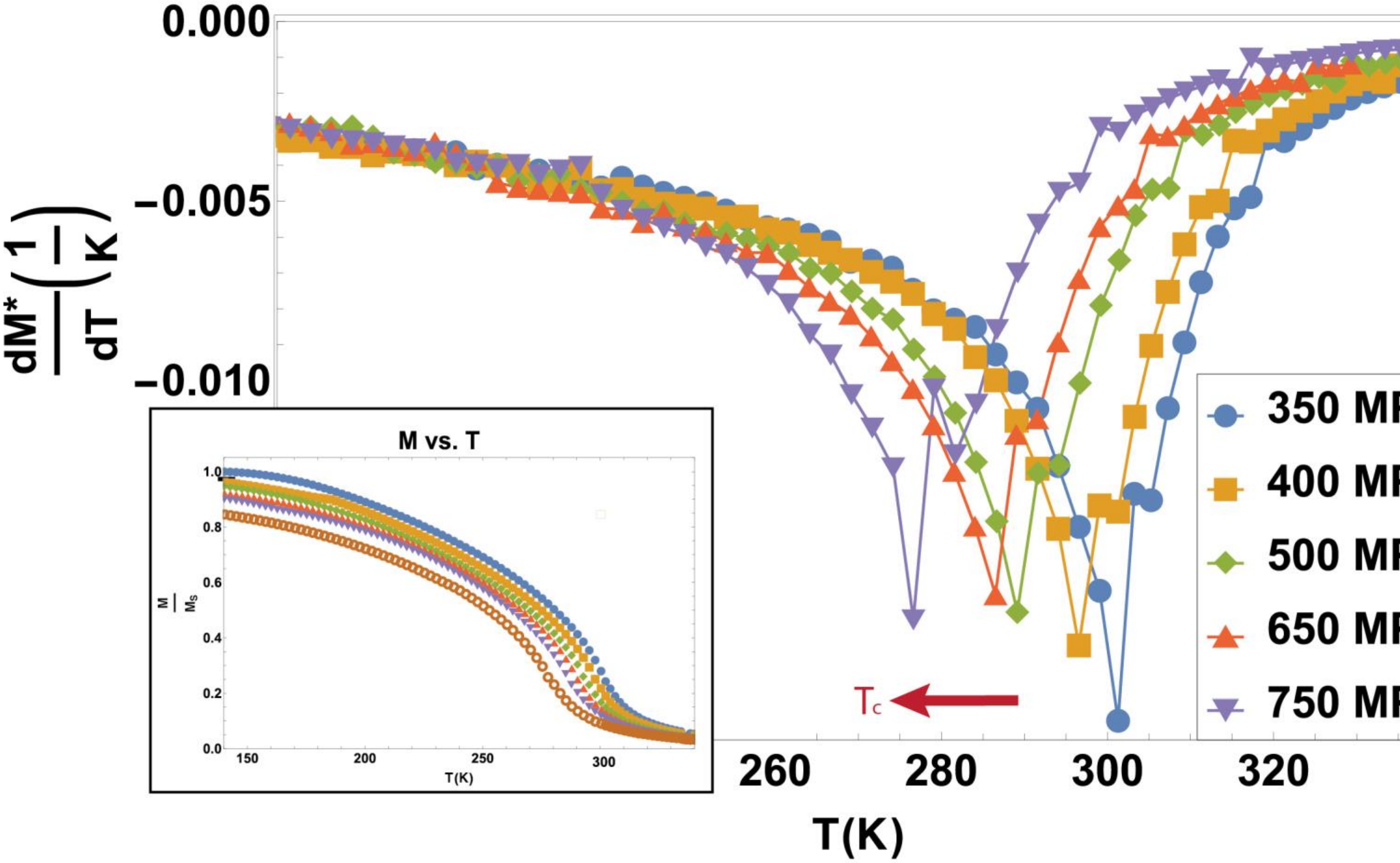
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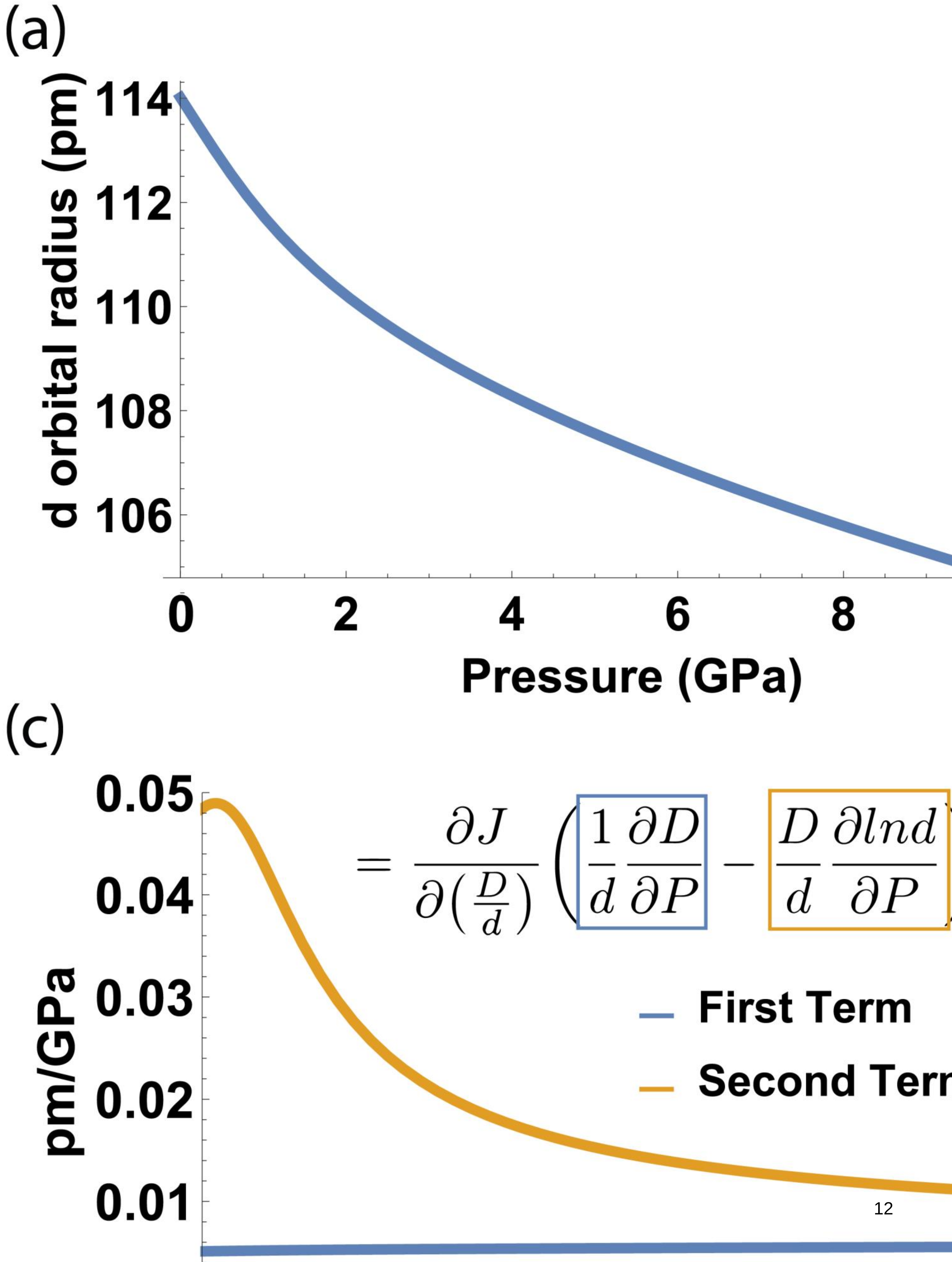
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