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Pressure dependence of $C_4N_2H_4$-mediated superexchange in $X\mathrm{Cl}_2(C_4N_2H_4)_2$ (X=Fe, Co, Ni)

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We present measurements of the magnetic susceptibility $\chi(T)$ on the pyrimidine bridged transition metal complexes $X\mathrm{Cl}_2(P)_2$ (X=Fe, Co, Ni; P=pyrimidine) under externally applied pressure. From our data we extract the pressure response of the antiferromagnetic phase transition at 6.4 K for X=Fe, 4.7 K for X=Co, and 16.3 K for X=Ni. The experiments indicate that with a pressure of ~8 kbar the transition temperature in all compounds increases by about 15%. Our data are complemented by electronic structure calculations, based on spin-unrestricted density functional theory. From these calculations we derive a bulk modulus B_0=20 GPa for $\mathrm{FeCl}_2(P)_2$, in reasonable agreement with the experimentally determined value of 15 GPa. Further, the calculations reproduce the antiferromagnetically ordered state as the ground state. Finally, we calculate the pressure response of T_N for $X\mathrm{Cl}_2(P)_2$, X=Fe, Ni, and derive an increase of T_N by 16% and 9% for Fe and Ni, respectively, in good agreement with the experiments.

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I. INTRODUCTION

In recent years, the subject of molecule-based magnetic materials has been the focus of very intense interdisciplinary research efforts.[1–5] In this field, one major driving force is the search for multifunctional materials, that is, compounds which combine useful magnetic properties with others, such as electrical conductivity or optical activity. While very many different materials have been produced by chemists working in this field, a comprehensive physical characterization, on a macro- and microscopical scale, has been carried out for only a few materials, and this mostly in context with quantum magnetism (see, for instance, the case of copper pyrazine dinitrate[6–11]). Materials with larger, i.e., classical spins have usually not been looked at in as much detail, although even for these systems there are various basic issues which are not well-understood so far.

In particular, the coupling between structural parameters and magnetic properties has been treated rather superficially. Molecule-based magnets, being structurally extremly soft, are very sensitive to the application of external pressure. This has been demonstrated, for instance, for purely organic molecule-based magnets.[12–14] In these organic radical compounds a ferro-to antiferromagnetic transition has been observed and tentatively attributed to a pressure induced change of the intermolecular interlayer interaction.[12] As yet, however, there is neither firm theoretical support nor direct experimental evidence for such a scenario.

Applying pressure to a molecule-based magnet affects its properties by variation of the distance between the magnetic ions and the geometry of the exchange path. Therefore, as we have demonstrated previously,[15,16] for understanding the effect of pressure on the properties of a given material, a detailed knowledge of the structural response is necessary. In those works we have presented qualitative arguments to explain the observed pressure effects in molecule-based magnetic materials. As yet, however, a comprehensive quantitative theoretical analysis is lacking. Therefore, here we present a detailed theoretical description of the experimentally determined structural and magnetic response of a series of molecule-based magnets to the application of hydrostatic pressure.

For our study we have investigated the transition metal coordination complexes $X\mathrm{Cl}_2P_2$, X=Fe, Co, Ni; P=pyrimidine=$C_4N_2H_4$. These materials crystallize in a tetragonal lattice of space group $I4_122$, as it is shown in Fig. 1, and with the tetragonal lattice parameters summarized in Table I.[17] The transition metal ions are connected via pyrimidine rings, thus forming a three-dimensional network of transition metal-pyrimidine complexes.

As a consequence of the structural three-dimensional (3D) network, a pyrimidine (N–C–N) mediated superexchange

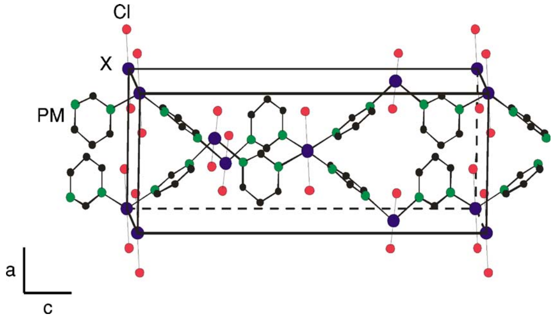

FIG. 1. (Color online) The tetragonal crystal structure of $X\mathrm{Cl}_2P_2$, X=Fe, Co, Ni; P=pyrimidine=$C_4N_2H_4$, space group $I4_122$.

TABLE I. The tetragonal lattice parameters of $X\mathrm{Cl}_2P_2$, $X=\mathrm{Fe,Co,Ni}$; $P=\text{pyrimidine}=\mathrm{C_4N_2H_4}$.

	a (Å)	c (Å)
FeCl_2P_2 (10 K)	7.368	20.339
CoCl_2P_2 (293 K)	7.419	19.935
NiCl_2P_2 (20 K)	7.349	19.529

yields magnetic coupling between the metal ions (Fig. 2), causing transitions into long-range magnetically ordered states at low temperatures.[17,18] The magnetically ordered structures for the three materials are canted antiferromagnetic below $T_N=4.7$ K ($X=\mathrm{Co}$), 6.4 K (Fe), and 16.3 K (Ni). The canting of the antiferromagnetic coupled moments, giving rise to a weakly ferromagnetic signal in susceptibility and magnetization experiments, has been studied in detail for FeCl_2P_2.[18] Here, an unusually large canting angle of 14° with a resulting ferromagnetic moment of 1 μ_B has been found and attributed to the interplay of antiferromagnetic exchange and single ion anisotropy on a crystallographic lattice with chiral symmetry.

We have performed measurements of the magnetization under external hydrostatic pressure up to 8 kbar on $X\mathrm{Cl}_2P_2$, $X=\mathrm{Fe,Co,Ni}$. For all three samples we find the transition temperatures to smoothly increase with pressure by about 15%. Complementary, we performed electronic structure calculations, in the framework of spin-unrestricted density functional theory. These calculations yield the bulk modulus B_0, the type of the magnetic ground state, and the pressure response of the magnetic transition temperatures. The calculated bulk modulus is derived as 20 GPa, which is in reasonable agreement with the value obtained experimentally for FeCl_2P_2, $B_0=15$ GPa.[15] Further, the calculations indicate that the pressure induced compression mostly acts on the electronic orbitals connecting the transition metal ions with the pyrimidine rings, while the rings themselves structurally are relatively inert. Moreover, from the calculations as stable magnetic ground state a superexchange-mediated antiferromagnetically ordered one is established. Finally, the calculations yield an increase of the magnetic transition temperatures for decreasing lattice parameters just at that rate which has been determined experimentally. Thus for the first time we have established the pressure response of a molecule-based class of magnetic materials both experimentally and theoretically.

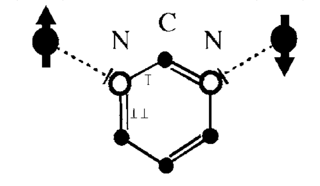

FIG. 2. The superexchange path between two transition metal ions $X=\mathrm{Fe,Co,Ni}$ along the pyrimidine backbone N–C–N in $X\mathrm{Cl}_2P_2$.

II. EXPERIMENTAL RESULTS

We have performed our magnetization (M) experiments under externally applied pressure in a commercial superconducting quantum interference device magnetometer. The measurements of $\chi(T)=M/H$ were carried out using a CuBe clamp type pressure cell at pressures up to ~8 kbar in the temperature range 2–300 K and in an external field of $H=200$ Oe. Polycrystalline powder $X\mathrm{Cl}_2P_2$, together with GE-Varnish, was pressed into pellets,[31] which were placed in the center of 7 cm long Teflon tubes. Each tube was filled with a hydraulic pressure medium (FC-77), sealed with CuBe pistons, and loaded into the pressure cell. The applied pressure was determined by measuring the superconducting transition temperature of a piece of indium,[19] which was placed inside, but at the end of the Teflon tube, via an ac-susceptibility measurement. This way, the experimental error for the pressure determination is about ±0.1 kbar.

In Fig. 3 we plot a set of representative measurements of the temperature dependence of the magnetic susceptibility $\chi(T)$ under externally applied pressure of $X\mathrm{Cl}_2P_2$. For FeCl_2P_2, at ambient pressure, the data nicely reproduces the behavior reported previously.[18] Here, in $\chi(T)$ a weakly ferromagnetic signal below $T_N=6.4$ K is observed, arising from the transition into the canted antiferromagnetic state. Similarly, at lowest experimentally applied pressure the magnetic susceptibilities of CoCl_2P_2 and NiCl_2P_2 reveal weak ferromagnetic ordering as the result of transitions into canted antiferromagnetic states below $T_N=4.7$ and 16.3 K, respectively, in perfect agreement with previous reports.[17]

With increasing pressure, as is shown in Fig. 3, magnetic ordering is stabilized for all three compounds. Specifically, for FeCl_2P_2 T_N increases from 6.4 K at ambient pressure to 7.4 K at 7.5 kbar (Fig. 3). Similarly, the antiferromagnetic transition temperatures T_N for CoCl_2P_2 linearily increase from 4.7 K at 1 bar to 5.4 K at 6.5 kbar, that of NiCl_2P_2 from 16.3 K at 1 bar to 17.9 K at 6.1 kbar[20] (Fig. 3). This is illustrated in Fig. 4, where we summarize the pressure dependence of the antiferromagnetic transition temperatures of $X\mathrm{Cl}_2P_2$, $X=\mathrm{Fe,Co,Ni}$, as obtained from our magnetization experiments under pressure.

All in all, there is a close resemblance of the pressure response for the three compounds. This is demonstrated in Fig. 5, where we now plot the normalized antiferromagnetic transition temperatures, $T_N/T_N(p=0)$, as a function of the normalized volume of the unit cell, $V(p)/V(p=0)$. Here, the dependence of the unit cell volume on pressure has been calculated on the basis of the data obtained for FeCl_2P_2,[15] which we assumed to be representative also for the other two compounds. We find that for a volume compression of about 5%, which with a bulk modulus $B=-V\Delta p/\Delta V=15$ GPa corresponds to an applied pressure of ~8 kbar, the antiferromagnetic transition temperatures of $X\mathrm{Cl}_2P_2$, $X=\mathrm{Fe,Co,Ni}$, increase by about 15%, with a fairly linear dependence of $T_N(V)$. We have previously demonstrated that this increase of T_N corresponds to a magnetic Grüneisen parameter $\Gamma_m=d(\ln(T^*/T_0))/d(\ln(V^*/V_0))$ of about 5.[15]

III. THEORETICAL CALCULATIONS

Qualitatively, our observation suggests that the orbital overlap along the superexchange path controls the antiferro-

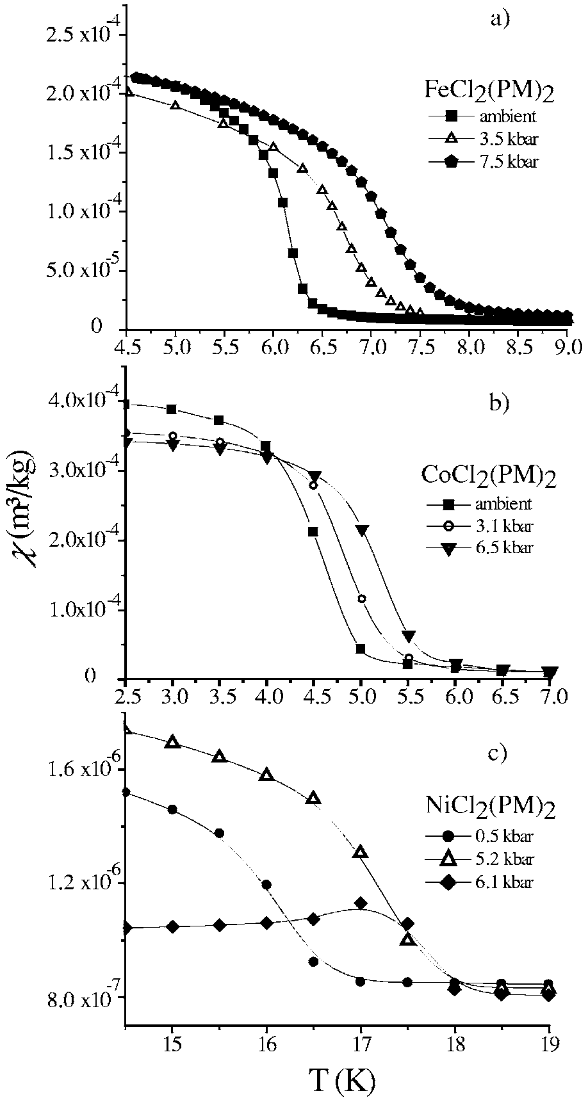

FIG. 3. The temperature dependence of the magnetic susceptibility $\chi(T)$ of $FeCl_2P_2$ (a), $CoCl_2P_2$ (b), and $NiCl_2P_2$ (c) in an external field of $H=200$ Oe under ambient and externally applied pressure. Lines are guides to the eye.

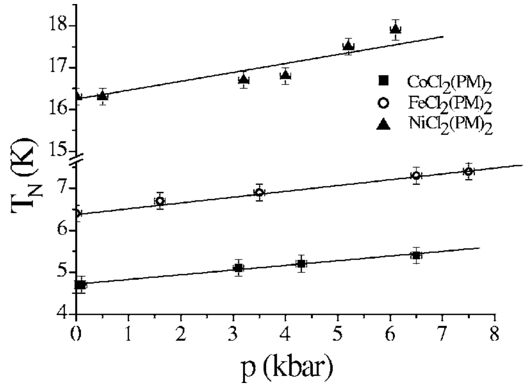

FIG. 4. The pressure dependencies of the antiferromagnetic transition temperatures of XCl_2P_2, X=Fe,Co,Ni. Lines are guides to the eye.

magnetic exchange in XCl_2P_2. In order to verify and quantify this model, we have carried out electronic structure calculations to establish the structural and magnetic pressure response of $FeCl_2P_2$ and $NiCl_2P_2$ from *ab initio* calculations. $CoCl_2P_2$ was not included in the calculations as this system is more difficult to treat. Especially, a reliable determination of the ground state configuration of the Co ion in this compound by density functional calculations was not possible. The ground state energies of the ferro- and antiferromagnetic state were computed in the framework of spin-unrestricted density functional theory, for different values of the cell parameter. The resultant solution of the Kohn-Sham equations is thus an eigenstate of S_z, but not of $\mathbf{S}^2$. The energy difference was therefore fitted to an Ising model, in order to estimate the exchange coupling J. In addition, for the system $FeCl_2P_2$, a geometry optimization of the fractional coordinates of the atoms in the unit cell was performed which was found to be necessary to compute the bulk modulus accurately. From these theoretical calculations we get a clear indication of which way the superexchange path (X–N–C–N–X) in the compounds is affected by the external applied pressure.

The calculations were done with the electronic structure code CRYSTAL.[23] Spin-unrestricted density functional calculations for the periodic system with the hybrid functional B3LYP (a mixture of Fock exchange, a modification of the Becke gradient corrected exchange functional, the Vosko-Wilk-Nusair local correlation functional, and the gradient corrected correlation potential by Lee, Yang, and Parr) were performed. The CRYSTAL code is based on local (Gaussian) orbitals. For $FeCl_2P_2$, the basis sets as in Ref. 18 were used, and in addition the nickel basis set was chosen as in Ref. 24.

First, the bulk modulus of $FeCl_2P_2$ was computed. Here, the iron ion is in a d^6 state, with the d_{xy} orbital doubly occupied, if we choose the geometry such that the neighboring nitrogen atoms are on the x and y axes, and the chlorine ions are on the z axis (this is a slight approximation as the angles are not exactly 90°). In a first attempt, this was done by fixing the fractional coordinates and changing the volume according to the ratio as it was observed experimentally[15] [i.e., at a pressure of 2.2 kbar, the $a(c)$ axis was reduced by 0.56 (0.35)%]. This ratio was fixed for the whole potential

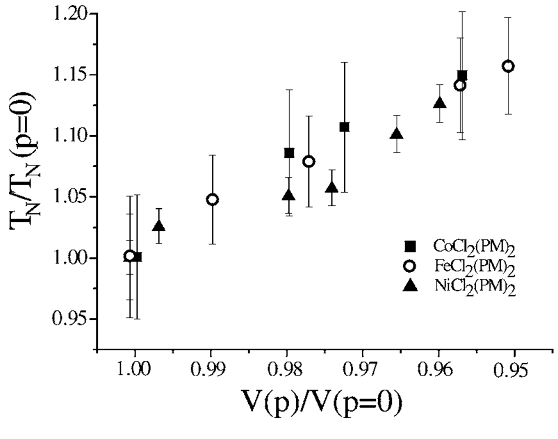

FIG. 5. The normalized antiferromagnetic transition temperatures $T_N/T_N(p=0)$ as a function of the normalized volume of the unit cell $V(p)/V(p=0)$ of XCl_2P_2, X=Fe,Co,Ni.

TABLE II. The computed bond lengths for various values of the cell parameters a and c. The experimental values are $a=7.3681$ Å and $c=20.339$ Å at 10 K and zero pressure (Ref. 18). To obtain the values under pressure, the experimental ratio for the compression along a and c from Ref. 15 was used. All values are at the B3LYP level. In the case of the N–C bond, the one along the N–C–N connection is the slightly shorter one (see Fig. 2).

a (Å)	7.0792	7.3681	7.5331
c (Å)	19.840	20.339	20.623
Fe—N	2.14	2.22	2.26
Fe—Cl	2.46	2.45	2.43
N—C (I)	1.33	1.34	1.34
N—C (II)	1.35	1.35	1.35
C—H	1.08	1.09	1.09
C—C	1.38	1.38	1.38

curve. It resulted in a good value for the equilibrium volume (1103 Å^3; experimental value: 1104 Å^3[18]), but an enormously large value of the bulk modulus (122 GPa) which is far beyond any error bar.

Therefore to accurately calculate the bulk modulus, it was necessary to optimize the fractional coordinates for various cell dimensions, thereby using the experimental value for the anisotropy of the compression, and to compute the bulk modulus from this pressure curve. Such an optimization can now be performed using the implementation of the analytical gradients in the CRYSTAL code.[25–27] This resulted in an equilibrium volume of 1114 Å^3 and a much smaller bulk modulus $B_0=20$ GPa, which is in reasonable agreement with the experimental value of 15 GPa.[15]

It is now interesting to study how the individual bond lengths change. From our calculations we find that the main change in the bond lengths occurs for the Fe–N bond. In contrast, all other bond lengths remain practically invariant, as can be seen in Table II. This observation explains why the approach of keeping the fractional coordinates fixed failed. Here, many bonds were artificially compressed which required too much energy and resulted in a too high value for the bulk modulus.

In a next step, the energies of the ferro- and antiferromagnetic state were computed for the various geometries (see Fig. 6). This property turned out to be fairly independent of the geometry optimization, i.e., it depends mainly on the dimensions of the cell, but changes only very little when the structural optimization of the fractional coordinates is performed.

First, we can compare the energy difference of the ferro- and antiferromagnet, which is 0.000188 E_h at zero pressure (equivalent to 59 K or 5.1 meV; 1 $E_h=1$ hartree $=315\,773$ K$=27.2114$ eV). In the following we use an Ising-like coupling, $H=-2\Sigma_{i<j}J_{comp}S_iS_j=-\Sigma_{i,j}J_{comp}S_iS_j$, in order to compute the magnetic coupling strength J_{comp}. The energy difference between ferromagnet and antiferromagnet ΔE, for a unit cell containing two magnetic ions would be J_{comp}, multiplied with the size of $S=2$ squared, the numbers of couplings ($z=4$, as each iron has four nearest iron neighbors), the number of iron atoms per cell (2, as the total energy is computed using a cell with 2 iron atoms), and another factor of 2 because the difference between ferromagnet, $S_iS_j=4$, and antiferromagnet $S_iS_j=-4$, is computed. We thus obtain: $\Delta E=-4J_{comp}zS^2=-64J_{comp}$, i.e., $J_{comp}\sim-3\mu E_h$ $=-0.9$ K. An estimate for the Néel temperature T_N (based on a mean field approximation, see, e.g., Ref. 28) would be $T_N=-\frac{2}{3}J_{exp}zS(S+1)$. A Néel temperature of 6.4 K and $S=2$ would thus result in $J_{exp}=-6.4\times\frac{3}{48}=-0.4$ K. The computed value thus agrees reasonably well with the experimental one, in particular considering that such an overestimation is not unusual with the B3LYP hybrid functional for exchange couplings.[29,30]

At $V(p)/V(p=0)=0.95$, the computed energy difference is around 0.000218 E_h (5.9 meV), i.e., we have an increase of 16% which is in reasonable agreement with the experiment (~15% increase).

For NiCl_2P_2, a similar study was performed. If again we arrange the cell in such a way that the nitrogen atoms are approximatively on the x and y axis, and the chlorine ions on the z axis, then the d_{xy}, d_{xz}, and d_{yz} orbitals are the doubly

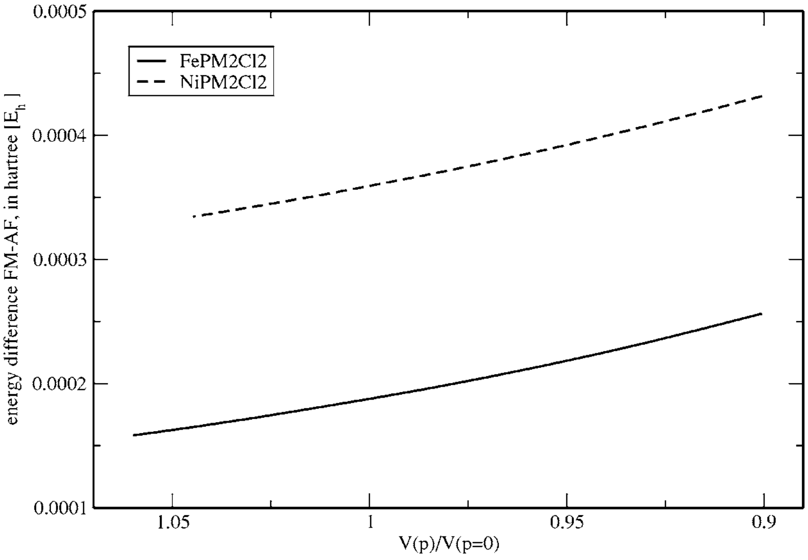

FIG. 6. Energy difference of the antiferromagnetic and ferromagnetic state of FeCl_2P_2 and NiCl_2P_2, plotted as a function of the normalized volume.

TABLE III. Mulliken populations and spin for $FeCl_2P_2$ and $NiCl_2P_2$, computed at the geometry corresponding to zero pressure.

	Fe	Cl	N	Fe	Cl	N
		Charge			Spin	
$FeCl_2P_2$	1.73	−1.07	−0.67	1.88	0.032	0.017
$NiCl_2P_2$	1.56	−1.06	−0.66	0.82	0.034	0.030

occupied d orbitals of the nickel ion (which is in a d^8 state). The superexchange was computed as a function of pressure. For this purpose, the unit cell was modified according to the experimental values for the compression in $FeCl_2P_2$ (see above). The fractional coordinates were not reoptimized, as in the case of $FeCl_2P_2$ this was found to be mandatory only for the calculation of the bulk modulus, but not for the energy difference of the ferro- and antiferromagnet. The results for $NiCl_2P_2$ are also displayed in Fig. 6.

A similar approximation as for $FeCl_2P_2$ would result in a value of $J_{exp}=-3$ K for $NiCl_2P_2$, using a spin $S=1$ and a Néel temperature $T_N=16.3$ K. At zero pressure, the energy difference between the ferro- and antiferromagnet is 0.000359 E_h (9.8 meV), resulting in a computed $J_{comp}=-22\mu E_h=-7$ K. The agreement between theoretical and experimental value again is reasonable. Also, at a compression of 5%, the energy difference increases by 9% to 0.000392 E_h (10.7 meV), which fully reproduces the experimental observation of an increase by ~10%.

Finally, in Table III the Mulliken populations are displayed. Iron and nickel are formally charged +2, although the actual charge is somewhat lower. The spin essentially resides on the iron and nickel ions, the neighboring chlorine ion and the nitrogens carry only little spin. This is also visualized in the spin density plot for the system $FeCl_2P_2$ (Fig. 7). The exchange path via the pyrimidine ring is visualized.

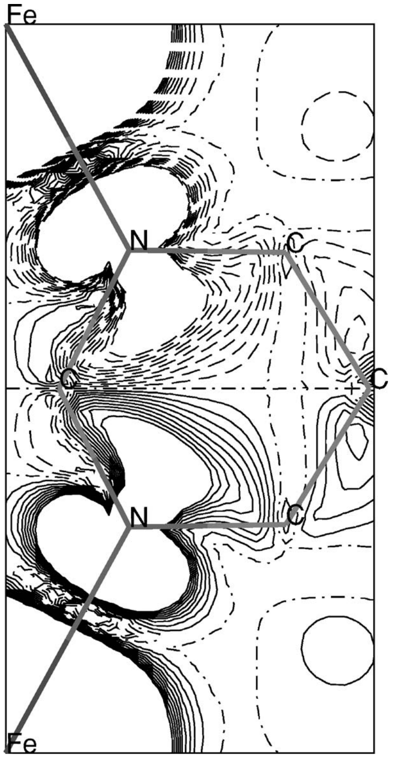

FIG. 7. Spin density plot of the system $FeCl_2P_2$, in the antiferromagnetic state. The spin density is plotted from −0.001 to $0.001|e|/\text{a.u.}^3$, in steps of 0.0001. Positive spin density is indicated with full lines, negative spin density with dashed lines, and zero spin density with dashed-dotted lines. The plane is chosen such that it contains the two iron atoms and the carbon atom on the right border.

IV. CONCLUSION

In conclusion, we have performed a pressure study on the antiferromagnetically ordered phases of the transition metal complexes $XCl_2(P)_2$, (X=Fe,Co,Ni; P=pyrimidine). We determine the pressure response of the antiferromagnetic transition temperature T_N, which for all three compounds increases by about 15% for a volume compression of ~5%. Our experimental data are complemented by electronic structure calculations on $XCl_2(P)_2$. These calculations yield good qualitative and quantitative agreement with respect to the response of the structural and magnetic properties of our systems. In particular, the calculations indicate that structurally the pyrimidine rings are not affected by externally applied pressure. Instead, the increasing antiferromagnetic transition temperature is caused by an enhanced orbital overlap of the $X-$N bond in this 3D-network system.

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