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Enhancement of antiferromagnetic coupling in the quasi-one-dimensional $Ca_3Co_2O_6$ ferrimagnet

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The magnetic coupling between quasi-one-dimensional ferromagnetic chains in $Ca_3Co_2O_6$ oxide has been studied using magnetic measurements under quasihydrostatic pressure (P) up to 12 kbar. It is found that the low-temperature ferrimagnetic phase, resulting from the antiferromagnetic coupling of ferromagnetic chains, is stabilized under pressure. Both the critical field for the spin-flip transition of the linear chains (H_{SF}) and the temperature T^* where the long-range ferrimagnetic ordering sets in rise under pressure with the following rates: $dH_{SF}/dP \approx 135-155$ Oe/kbar and $dT^*/dP \approx 0.073$ K/kbar, respectively. We show that these variations can be accurately described in terms of the interchain bond-length compression.

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The study of the magnetic properties of low-dimensional magnetic systems has been a subject of interest for a long time; particularly those exhibiting a transition to a three-dimensional (3D) ordered state.[1,2] Among the compounds having such a particular phenomenology, the quasi-one-dimensional (1D) systems have attracted much attention since it is the easiest to analyze.[2–6] In this case, a 3D transition can be eventually induced by the weak interactions between chains of ferromagnetically coupled spins. Prototypical examples of the latter group are ABX_3 type compounds, such as the case of $CsCoCl_3$ and $RbFeCl_3$ extensively studied in Ref. 2.

The compound $Ca_2Co_3O_6$, subject of this study, also belongs to these kind of 1D systems having a 3D ordered state at low temperatures. This compound adopts the K_4CdO_6 structure[7] ($R\overline{3}c$). The basic network is a c-axis oriented hexagonal arrangement of chains, which form a triangular lattice in the ab plane. The chains are made of alternating face-sharing CoO_6 octahedra [antitrigonal prism, labeled as (Co1) position] and CoO_6 trigonal prisms [labeled as (Co2) position]. The atomic spins in the chains are ferromagnetically (F) coupled along the hexagonal c axis thus forming a quasi-1D system. Interchain magnetic coupling is antiferromagnetic (AF), and thus in the ab-plane triangular lattice there may exist some degree of frustration.[6]

The magnetic properties of this compound[3–6] can be summarized as follow: at high temperatures the sample shows paramagnetic behavior, as temperature decreases intrachain F interactions start to appear below about 80 K. F ordering inside the chains is reached at $T_C \approx 30$ K,[4,5] on decreasing further the temperature the onset of AF interchain interactions is indicated by an abrupt increase of the susceptibility at T_N. The ferrimagnetic (FM) ordering in a triangular lattice is reached at $T^* < T_N$ as indicated by a cusp in the magnetic susceptibility. A distinctive signature of the ferrimagnetic ordering is the plateau observed in the magnetization versus field curves at $\sim\frac{1}{3}$ of the saturation magnetization.[5,6] When increasing further the magnetic field, a spin-flip transition, or metamagnetic transition, is observed at a critical field value (H_{SF}) at which the magnetization suddenly rises up to its saturation value. The saturation magnetization observed at $H > H_{SF}$ clearly indicates a complete ferromagnetic ordering of all magnetic moments. Thus the magnetization observed for $H < H_{SF}$ is consistent with a ferrimagnetic ordering of quasi-1D ferromagnetic chains. For temperatures below 10 K the plateau becomes shadowed and the $\frac{1}{3}$ relation does not hold any longer indicating that more complicated arrangements than the simplest triangular lattice are present in this low-temperature regime.[8]

In this paper we will show that the interchain antiferromagnetic coupling in $Ca_3Co_2O_6$ can be conveniently modified by applying an external pressure (P). We will show that the AF interactions are reinforced and thus the stability range of the ferrimagnetic ordering broadens. Quantitative analysis of the variations of the spin-flip field H_{SF} and the ferrimagnetic ordering temperature T^* under pressure (dH_{SF}/dP and dT^*/dP) reveals that bond-length contraction is the primary mechanism for these variations.

$Ca_3Co_2O_6$ sample preparation was described in Ref. 3. The average cationic composition was established by inductive plasma coupling, while the local composition in single crystallites was determined by energy dispersive spectroscopy (EDS). Results were found consistent with the nominal composition. The oxygen content was determined by thermogravimetry after reduction under H_2/He atmosphere and was also in agreement with the nominal composition. Powder x-ray diffraction patterns, can be indexed on the basis of a rhombohedral unit cell ($R\overline{3}c$) (Ref. 3) with parameters $a = 9.07$ Å and $c = 10.38$ Å. Electron diffraction patterns and high resolution images[9] show a complete ordering of the octahedra and prismatic building-block units.

dc magnetic properties were measured by using a commercial SQUID magnetometer up to 55 kOe and extraction magnetometery up to 80 kOe. ac susceptibility was also measured in a PPMS susceptometer. Pressure-dependent susceptibility measurements were done under a quasi-hydrostatic

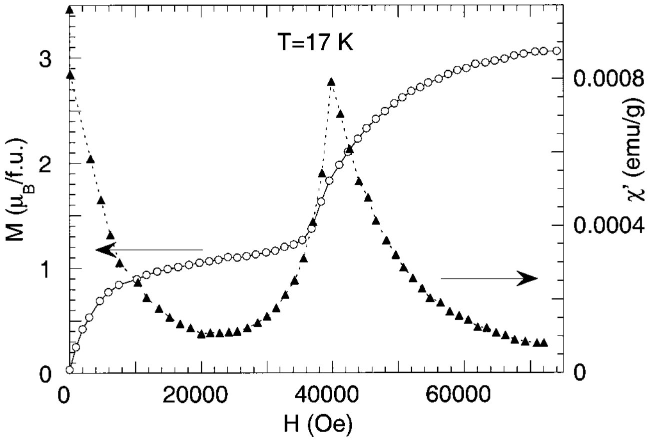

FIG. 1. Magnetization curve and ac susceptibility $\chi'(H)$ curve measured using a driving field amplitude of $h_{ac}=1$ Oe and frequency $v=10$ kHz at $T=17$ K. A sharp peak in $\chi'(H)$ is observed at H_{SF}.

pressure, by using a clamp-type piston-cylinder cell adapted for the PPMS, with an organic liquid as pressure-transmitting medium, taking into account the decrease of pressure when cooling.

The basic magnetic characterization of the sample can be found in Refs. 1, 6, and 10. The experimental data roughly obey a Curie-Weiss law at high temperatures (above about 80 K) giving a extrapolated Curie temperature $\theta \approx 33$ K, confirming the *F* nature of spin interactions inside the chains, and an effective paramagnetic moment per formula unit (f.u.) of $\sim 3.9\,\mu_B$/f.u. The onset of AF interactions between chains is identified by the abrupt upturn of the susceptibility at about $T_N \approx 25$ K. On lowering temperature, the dc susceptibility describes a peak at about $T^* \approx 13$ K that is identified as the temperature at which the long-range triangular FM order is established over the sample.

A quantitative analysis of the susceptibility by using the following equation:

$$\chi_{\parallel}=\frac{2Ng_{\parallel}^2\mu_B^2}{kT[\exp(D/kT)+2]-8J_{\parallel}}, \tag{1}$$

where *D* is the single-ion anisotropy,[11] as suggested in Refs. 1, 10, 6 has been performed. This fit allows determining the *g* factor as well as *D* and the exchange interaction $J_{\parallel}$. The values obtained are $J_{\parallel}/k \approx 3.1$ K, $D/k \approx -227$ K, and $g_{\parallel} \approx 3.75$. The large value of $g_{\parallel}$ is attributed to the large single-ion anisotropy. The positive value of $J_{\parallel}$ is an indication of the *F* character of intrachain interactions. The extracted $J_{\parallel}$, *D*, and $g_{\parallel}$ values are in rough agreement with those reported in Ref. 6. The differences can be understood taking into account that our measurements have been performed in a nonoriented powder sample.

As shown in Fig. 1 a well-defined step exists in the $M(H)$ curves, at some intermediate temperatures below $T_N \approx 23$ K. The magnetization at the plateau is about $1.2\,\mu_B$, and at $H_{SF} \approx 35$ kOe the magnetization suddenly rises up to about $3.3\,\mu_B$ at ~80 kOe, i.e., the magnetization at the plateau, below H_{SF} is $\sim\frac{1}{3}$ of the maximum value. This is just as expected for a ferrimagnetic arrangement of ferromagnetic chains in a triangular lattice. As temperature increases the AF interactions between chains become weaker and the plateau and the jump in the magnetization are progressively smeared out. At temperatures below 10 K, the next-nearest-neighbor interactions become more and more important and the triangular FM ordering is replaced by more complicated arrangements of the chains.[8,12]

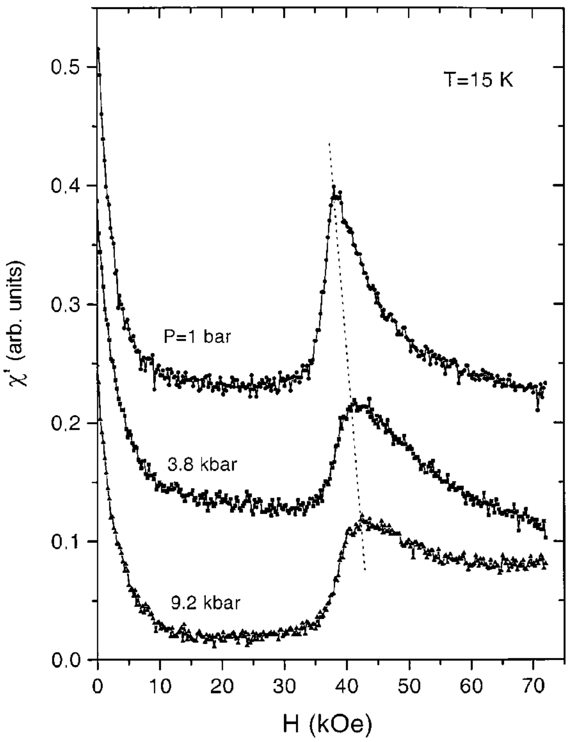

FIG. 2. Field dependence of χ' at three different pressures at a constant temperature $T=15$ K and a driving field amplitude of $h_{ac}=0.1$ Oe and frequency $v=77$ Hz.

The magnitude of the spin-flip field H_{SF} is a measure of the interchain AF interactions, therefore it can be used to monitor the strength of the AF coupling. It is worth mentioning here that H_{SF} can be easily determined by measuring the real part of the ac susceptibility as a function of the applied dc magnetic field $\chi'(H)$. As illustrated in Fig. 1, $\chi'(H)$ describes a sharp peak on crossing the critical field H_{SF}. We will take advantage of the sharpness of this peak to check the stability under pressure of the triangular FM arrangement of *F* chains.

In Fig. 2 we show the dc field dependence of χ' for several applied pressures at a given temperature (15 K). An upward shift of H_{SF} is observed as quasihydrostatic pressure increases, therefore implying that the FM ordering between chains are reinforced under pressure. Similar results are observed at other temperatures where a magnetization jump and a peak in χ' could be observed. These results are collected in Fig. 3(a) for several temperatures. We note that $dH_{SF}/dP \approx 135-155$ Oe/kbar.

We have also analyzed the pressure dependence of the AF interactions by measuring $\chi'(T)$ at different pressures. As mentioned above, both T^* and T_N are related to the strength of the interchain AF interactions. However, the sharpness of

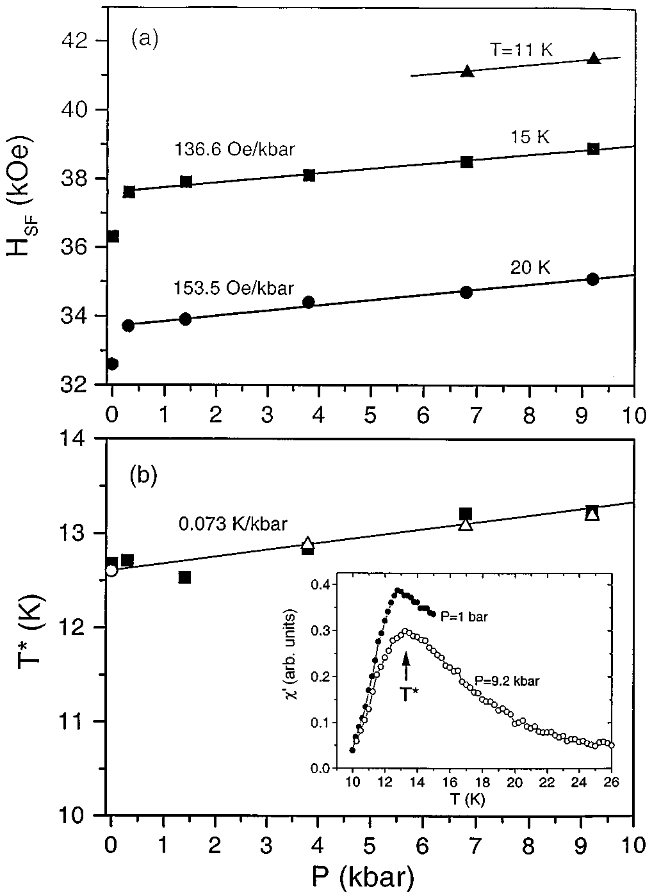

FIG. 3. (a) Pressure dependence of the spin-flip H_{SF} at several temperatures. (b) Pressure dependence of long-range ferrimagnetic ordering temperature T^*. Distinct symbols corresponds to data taken from different temperature sweeps. Inset: Temperature dependence of the magnetic susceptibility at two distinct pressures.

T^* leads to a more precise determination of any shift under pressure [see inset of Fig. 3(b)]. A clear rising of T^* can be observed, which signals that the AF interactions becomes reinforced under pressure. The $T^*(P)$ values are collected in the main panel of Fig. 3(b). To illustrate the experimental reproducibility, data from two different temperature sweeps are shown. It turns out that $dT^*/dP \approx 0.073\,\mathrm{K/kbar}$.

In order to obtain quantitative estimate of the measured pressure dependence of the Néel temperature T_N, or T^*, and the spin-flip field H_{SF}, we proceed as follows. Very generally it can be written that $T_N \sim T^* \sim J_{\mathrm{AF}}$, where J_{AF} stands for the antiferromagnetic interchain coupling interaction. The superexchange interactions are known to be strongly dependent on the coupling bridge length (l), typically $J_{\mathrm{AF}} \sim (1/l)^n$ with $n \sim 12$.[13] In the present case l should be associated to the interchain distance. On the other hand, the spin-flip critical field H_{SF} being a measure of the antiferromagnetic coupling between quasi-1D ferromagnetic chains, can also be written as $H_{\mathrm{SF}} \sim J_{\mathrm{AF}}$ and accordingly $H_{\mathrm{SF}} \sim (1/l)^n$. Therefore:

$$\frac{d\ln T^*}{dP} \approx \frac{d\ln H_{\mathrm{SF}}}{dP} = -\frac{n}{l}\,\frac{dl}{dP}. \qquad (2)$$

In order to use Eq. (2) to get an estimate of the predicted variations of T^* and H_{SF} under pressure, an estimate of the bondlength compressibility modulus $\kappa = -(1/l)(dl/dP)$ is required. We are not aware of high-pressure studies in this family of oxides, and so the κ values are not known. In order to get a rough estimate we can use the compressibility modulus measured in other transition metal perovskites. To this regard, the series $\mathrm{LnNiO_3}$ ($\mathrm{Ln} = \mathrm{La, Pr, Nd}, \ldots$) is very convenient as it has been particularly well studied and the corresponding κ values could be used. According to Medarde *et al.*,[14] it turns out that $\kappa \approx -4.4 \times 10^{-4}\,\mathrm{kbar}^{-1}$ for $\mathrm{PrNiO_3}$.[14] Using this value of κ to estimate $d\ln T^*/dP$ and $d\ln H_{\mathrm{SF}}/dP$ we obtain $d\ln T^*/dP \approx d\ln H_{\mathrm{SF}}/dP \approx 5.3 \times 10^{-3}\,\mathrm{kbar}^{-1}$.

We note that this rough evaluation, leads to values that are in excellent agreement with the experimental data: $d\ln T^*/dP \approx 5.6 \times 10^{-3}\,\mathrm{kbar}^{-1}$ and $d\ln H_{\mathrm{SF}}/dP \approx 4 \times 10^{-3}\,\mathrm{kbar}^{-1}$. This illustrates that the rising of both T^* and H_{SF} under pressure can be, not only qualitatively but also quantitatively understood, on the basis on the reinforcement of the AF coupling between chains under pressure.

In summary, we have reported data about the pressure dependence of the AF interactions between chains and the stability of the FM triangular phase under pressure. It is found that both the spin-flip field and the ferrimagnetic ordering temperature rise under pressure, thus indicating that the interchain AF interactions are reinforced under pressure. Consequently, the FM triangular arrangement occurs at higher temperature and extends in a broader temperature range.

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