补充材料

锌离子掺杂钴基金属有机材料$[(CH_3)_2NH_2]Co_{1-x}Zn_x(HCOO)_3$中的低温反常磁现象

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第一部分：单晶四圆衍射晶格常数结果

Part 1. Lattice constants of four-circle single-crystal diffraction

表 S1 不同掺杂比例样品单晶衍射分析得到的晶格常数

Table S1. Lattice constants of samples with different proportions.

Crystal type	$a=b$/Å	c/Å
DMCoF (theory)	8.2062	22.2960
DMCoF	8.2032	22.2652
$DMCo_{0.9}Zn_{0.1}F$	8.2057	22.244
$DMCo_{0.8}Zn_{0.2}F$	8.1966	22.2612
$DMCo_{0.7}Zn_{0.3}F$	8.1964	22.236
$DMCo_{0.6}Zn_{0.4}F$	8.179	22.23
$DMCo_{0.5}Zn_{0.5}F$	8.1948	22.2408
DMZnF (theory)	8.1924	22.277

第二部分：EDS 分析结果和元素分布图

Part 2. EDS analysis results and element distribution map

表 S2 $DMCo_{1-x}Zn_xF$ 单晶样品中 Co, Zn 原子比例 EDS 测量结果

Table S2. EDS measured atomic proportions of Co and Zn for $DMCo_{1-x}Zn_xF$.

	Co/Zn atomic percent/%	
Normal ratio *x*	Co	Zn
0.1	94.817	5.183
0.2	83.245	16.755
0.3	83.860	16.140
0.4	80.721	19.279
0.5	70.143	29.857

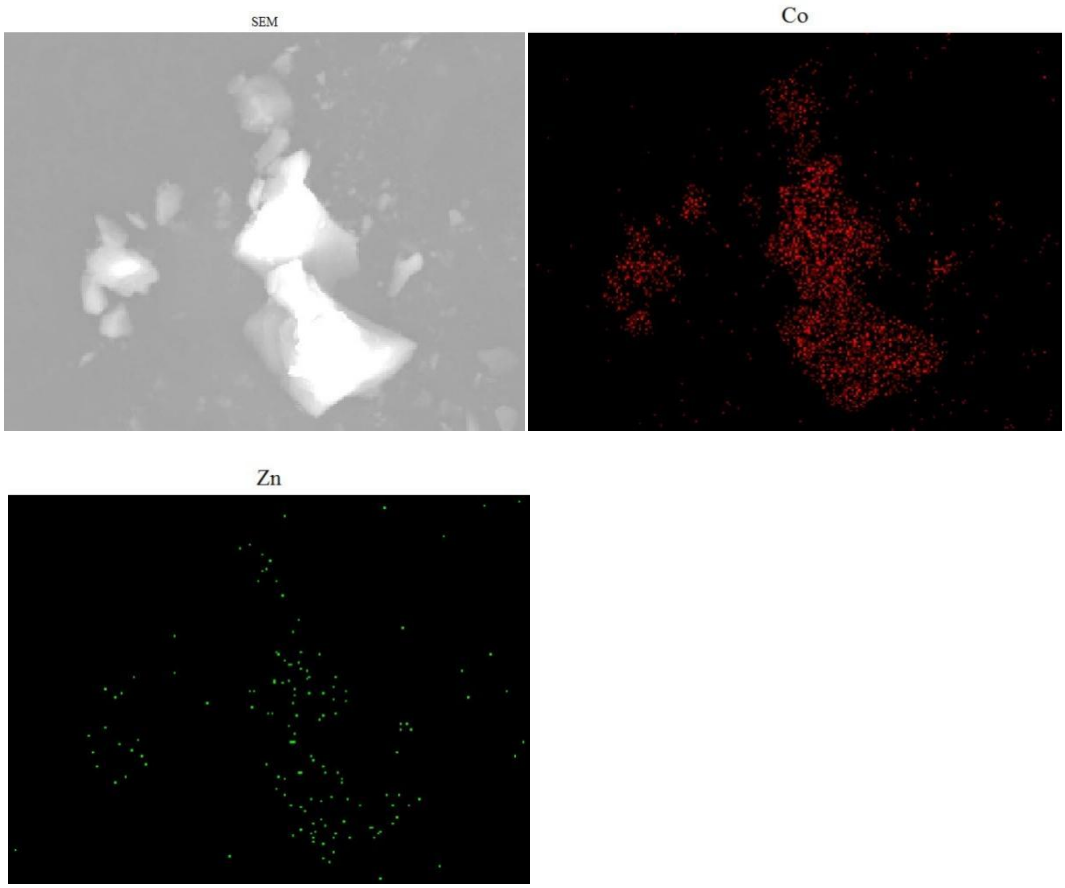

图 S1 $DMCo_{0.8}Zn_{0.2}F$ 样品的扫描电子显微镜形貌图和 Co, Zn 元素分布图, 其中红色是 Co 原子, 绿色是 Zn 原子

Fig. S1. Scanning electron microscope (SEM) image and colour coded SEM/EDX dot maps of Co (red) and Zn atoms (green) of sample $DMCo_{0.8}Zn_{0.2}F$.

第三部分：掺锌样品低温磁性测量结果

Part 3. Low-temperature magnetic measurement results of zinc doped samples

(a) (b)

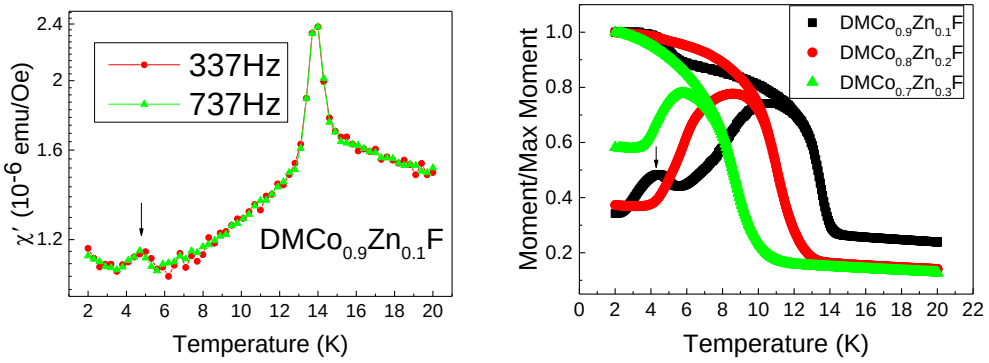

图 S2 (a)低温下零场时，$DMCo_{0.9}Zn_{0.1}F$ 样品交流磁化率随频率和温度的变化曲线; (b) 不同掺锌比例样品在 0.1 T 外场下场冷和零场冷曲线。

Fig. S2. (a) Temperature dependence of susceptibility χ' of DMCo0.9Zn0.1F single crystal at different frequencies; (b) curves of magnetization versus temperature measured in 0.1 T with both ZFC and FC modes for Zn doped samples with doping ratio x=0.1, 0.2, 0.3.

图 S2 (a)所示为 $DMCo_{0.9}Zn_{0.1}F$ 样品交流磁化率随温度的变化曲线，在不同频率下，14 K 附近都有反铁磁相变引起的弛豫峰。在更低的温度下，5 K 附近也观察到了一个弱的峰，由于信号非常微弱，不能仔细分析这一弛豫峰对频率的依赖关系（更低频率的信号由于噪声很大，没有放在图上）. 对比田英等[S1]在铁基体系中的结果，这一体系可能在更低频率下才有明显的磁响应. 交流磁响应受到交直流磁场的大小、频率，以及体系的晶向、对称性等许多因素的影响，对 Co 基掺杂体系磁弛豫的研究还有待于后续系统的分析.

Figure S2(a) shows the curve of AC magnetic susceptibility versus temperature of $DMCo_{0.9}Zn_{0.1}F$ sample. At different frequencies, relaxation peaks caused by antiferromagnetic phase transitions are found around 14 K. A weak peak is also observed near 5 K at lower temperatures, and the frequency dependence of this relaxation peak cannot be carefully analyzed because the signal is very weak (the lower frequency signal is not shown in the figure due to high noise). Compared with the results of Tian Ying et al.[S1] in the iron-based system, the system may have an obvious magnetic response at a lower frequency. The AC magnetic response is affected by many factors, such as the size and frequency of the AC and DC magnetic fields, as well as the crystal orientation and symmetry of the system. The study of magnetic relaxation of the Co-doped

system remains to be analyzed in the subsequent system.

图 S2 (b) 分别给出了掺杂比例分别为 x=0.1，0.2，0.3 样品在 0.1 T 磁场下的零场冷(ZFC)和场冷曲线，可以看到，$DMCo_{0.9}Zn_{0.1}F$ 的 ZFC 曲线中除了反铁磁相变引起的在 14 K 附近反常增加以外，在低温 5 K 附近有一个反常增加，这有可能是由于在这一温度区间存在磁单离子和长程反铁磁相互作用的竞争，使得体系的宏观磁矩发生反转. 在掺锌浓度更高的样品中这一现象并不太明显，样品的宏观磁矩在低温下略有增加，体系中两种磁行为的竞争可能在更低的温度下进行。

Figure S2(b) shows the zero-field cold-field cold curves of samples with doping ratio x=0.1, 0.2 and 0.3 respectively under a magnetic field of 0.1 T. It can be seen from the figure that in the ZFC curve of $DMCo_{0.9}Zn_{0.1}F$, there is an abnormal increase near 14 K, caused by the antiferromagnetic phase transition, and there is an abnormal increase near 5 K at low temperature. This may be due to the competition between magnetic single ions and long-range antiferromagnetic interactions in this temperature range, resulting in the reversal of the macroscopic magnetic moment of the system. This phenomenon is not obvious in the samples with higher zinc concentrations. The macroscopic magnetic moments of the samples increase slightly at low temperature, and the competition between the two magnetic behaviors in the system may take place at lower temperature.

图 S3 所示为对 $DMCo_{0.9}Zn_{0.1}F$ 样品在共振场处不同温度下的磁弛豫测量结果，具体测量步骤如下：先将样品加到高场 3 T，再将磁场降到共振场位置，扫时间测样品磁矩随时间的变化。分别测量了 2 K 和 8 K 时第一个台阶附近－0.18 T 时样品磁矩随时间的变化关系，数据进行了归一化处理。2 K 数据可以用 $\exp(-t^{0.5}\times0.06174)$较好拟合，8 K 数据用 $\exp(-t\times0.0022)$较好拟合。

Figure S3 shows the magnetic relaxation measurement results of $DMCo_{0.9}Zn_{0.1}F$ sample at different temperatures in a resonance field. The specific measurement steps are as follows. First, the sample is added to a high field of 3 T, and then the magnetic field is lowered to the resonance field position. The variation of the magnetic moment of the sample with time at －0.18 T near the first step at 2 and 8 K are measured respectively, and the data are normalized. For 2 K data, $\exp(-t0.5\times0.06174)$ can be used for better fitting, and for 8 K data, $\exp(-t\times0.0022)$ can be used for better fitting.

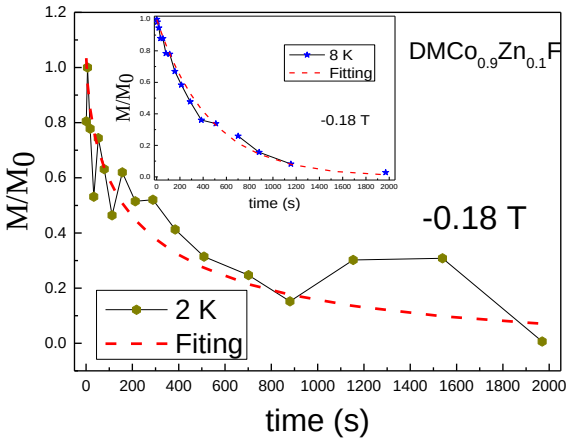

图 S3　2 K 和 8 K 时，$DMCo_{0.9}Zn_{0.1}F$ 样品在共振场-0.18 T 时的磁弛豫测量结果，点线为拟合结果。

Fig. S3. Magnetic relaxation results of $DMCo_{0.9}Zn_{0.1}F$ sample measured at 2 K (8 K in insert) in 0.18 T magnetic field.

参考文献

[S1] Tian Y, Wang W, Chai Y, Cong J, Shen S, Yan L, Wang S, Han X, Sun Y 2014 *Phys. Rev. Lett.* **112** 017202