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Superparamagnetic relaxation in $\mathrm{Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4}$

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$\mathrm{Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4}$ has been studied by Mössbauer spectroscopy, x-ray diffraction, and magnetic measurements. The crystal structure is found to be a cubic spinel with the lattice parameter $a_0=9.917$ Å. Absence of quadrupole splitting suggests that iron ions occupy only tetrahedral sites. It is notable that as the temperature increases toward the Néel temperature, $T_N=252$ K, line broadening and a pronounced central peak appear, suggesting superparamagnetic relaxation. The temperature dependence of the effective anisotropy energy is also found to decrease rapidly with increasing temperature, thereby supporting the observed rapid increase of the superparamagnetic relaxation rate below T_N.

In the last twenty years, the sulphospinels AB_2S_4, where A and B are metals, have been extensively studied and a large variety of magnetic properties have been reported.[1] However, papers on relaxation effects in these materials are rare.[2]

Line broadening and the presence of a pronounced central peak have been observed in ^{57}Fe Mössbauer hyperfine spectra of both fine particle[3,4] and bulk samples[5] and interpreted as arising from superparamagnetic relaxation. The spin-flip process[6] of the magnetic moment in superparamagnetic fine particles is described by a flip frequency f of

$$f=f_0\exp(-KV/k_BT)\,, \tag{1}$$

where f_0 is a frequency factor of the order of 10^9 s^{-1}, whose origin is in random thermal effective torques or fields. K is the effective anisotropy energy per unit volume, and V the particle volume. As the temperature is raised to the magnetic-ordering temperature, K is shown to decrease to zero,[7] and in that case it is expected from Eq. (1) that f will increase rapidly and thus, reversal of magnetization over comparatively large volumes can be thermally activated.

The purpose of this paper is to report Mössbauer and x-ray measurements for $\mathrm{Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4}$ with special emphasis on the superparamagnetic relaxation observed below the Néel temperature.

A $\mathrm{Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4}$ sample was prepared by direct reaction of the elements in a sealed quartz tube at 1050 °C for 10 days. X-ray-diffraction patterns showed that the sample has the cubic spinel structure. The lattice parameter a_0 was found to be 9.917 ± 0.002 Å by plotting $a_0(\theta)$ against the Nelson-Riley function[8] and extrapolating to $\theta=90°$.

Mössbauer spectra of the sample were measured at various absorber temperatures. Some of them are shown in Figs. 1 and 2. The Mössbauer absorption lines are six in number and are sharp at 80 and 120 K. They become broader with increasing temperature until a pronounced central peak appears near 239 K, suggesting the appearance of superparamagnetic relaxation. The Mössbauer spectrum at 80 K has been analyzed by a least-squares fitting to six Lorentzian lines with the help of a computer, and the following parameters are found: the magnetic hyperfine field $H=373\pm2$ kOe; the quadrupole shift $E_Q'=1/4(V_1-V_2-V_5+V_6)=-0.009\pm0.005$ mm/s, where V_i represents the position of the ith absorption line; the isomer shift relative to the Fe metal, $\delta=0.449\pm0.005$ mm/s.

The vanishing quadrupole splitting suggests that iron ions occupy the tetrahedral sites in the spinel structure be-

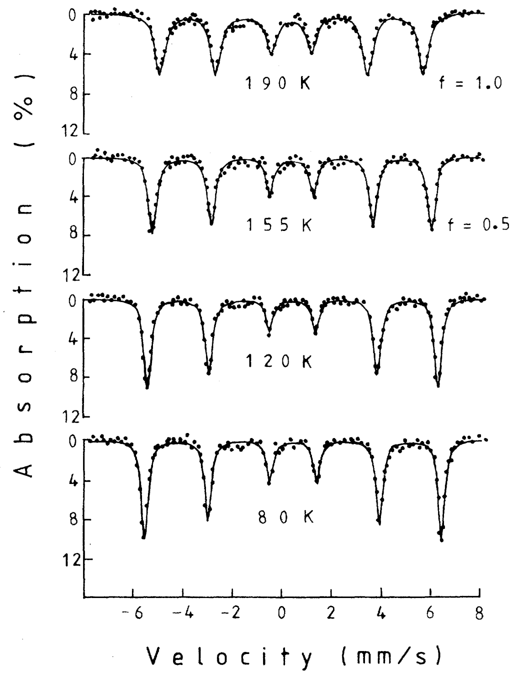

FIG. 1. Mössbauer spectra of $\mathrm{Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4}$ at low temperatures. The relaxation frequency f is in units of $\Gamma/\hbar$.

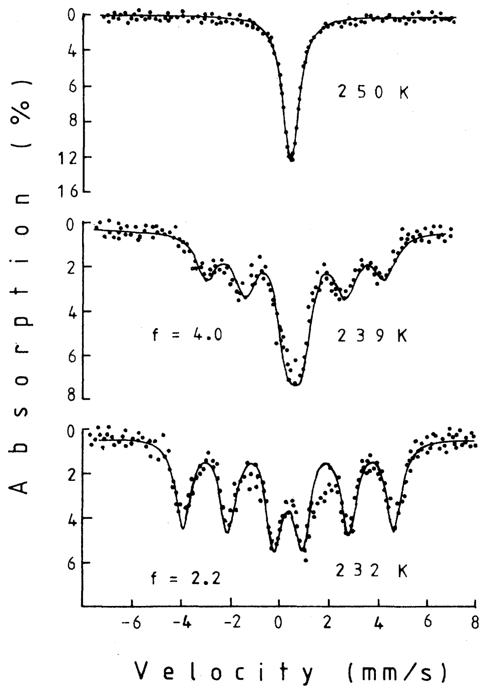

FIG. 2. Mössbauer spectra of $Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4$ just below the Néel temperature.

cause the local symmetry of a tetrahedral site is cubic T_d while that of an octahedral site is trigonal D_{3d}.

In order to explain the line broadening and appearance of a central peak observed above about 150 K in terms of superparamagnetic relaxation, let us use the following expression[9] derived by Blume and Tjon for the line shape of the Mössbauer emission (or absorption) spectra in the presence of a fluctuating magnetic field which jumps between the values $+H$ and $-H$ along the z axis with a frequency f:

$$W(k)=\frac{2}{\Gamma}\mathrm{Re}\sum_{m_0 m_1}\tfrac{1}{4}\,|\langle I_0 m_0|H^{(+)}|I_1 m_1\rangle|^2 \times\sum_{i,j}\tfrac{1}{2}\langle j|(P-W-i\alpha F)^{-1}|i\rangle\,, \tag{2}$$

where

$$P=-i(\omega-\omega_0)+\tfrac{1}{2}\Gamma\,,$$

$$\alpha=(g_0 m_0-g_1 m_1)\mu H\,,$$

$$W=\begin{bmatrix}-f & f\\ f & -f\end{bmatrix},$$

and

$$F=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}.$$

Here $H^{(+)}$ is the operator for emission of a gamma ray by the nucleus. Γ is the natural linewidth, ω and **k** are the frequency and wave vector of the gamma photon. $|I_0 m_0\rangle$ and $|I_1 m_1\rangle$ ($m_0=\pm\frac{1}{2}, m_1=\pm\frac{1}{2},\pm\frac{3}{2}$) represent the ground and the first excited states of ^{57}Fe, respectively. g_0 and g_1 are the g factors of the ground and the first excited states of ^{57}Fe, μ is the nuclear magneton, and ω_0 is the frequency of the unsplit line for ^{57}Fe.

Since the above expression shows only the emission (or absorption) probability, it is necessary to carry out the integration

$$a(v)=\int_{-\infty}^{\infty}W(\omega)F[\omega-\omega_0-(\omega_0/c)v]d\omega \tag{3}$$

in order to fit the theoretical curve to the Mössbauer spectra. $F(x)$ is a single-line source spectrum, c is the velocity of light, and v is the Doppler velocity of the source. The line-shape function $A(v)$ was calculated for each Doppler velocity v using a computer, and the results are shown as solid lines through the data points in Figs. 1 and 2 with corresponding f values. The relaxation rate f increases rapidly as the temperature approaches the Néel temperature of 252 K.

In order to have a plausible explanation for the origin of the rapid increase in f, the temperature dependence of the effective anisotropy energy K was determined by measuring the work necessary to magnetize the sample from its demagnetized state to the saturated state by an external field H:

$$W=\int_0^{M_s}HdM\,, \tag{4}$$

where M_s is the saturation value of the magnetization. The work W is expected to be proportional to the effective anisotropy energy K. Figure 3 shows that the work W or the anisotropy energy K decreases rapidly as the temperature approaches the Néel temperature, thereby explaining the observed rapid increase in the relaxation frequency indicated by Eq. (1).

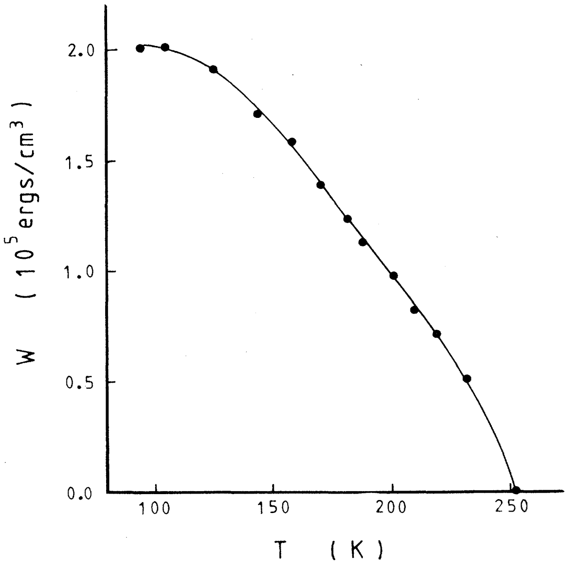

FIG. 3. Temperature dependence of the effective anisotropy energy for $Co_{0.7}Cu_{0.15}Fe_{0.15}Cr_2S_4$. W was determined by integrating the magnetization curve along the magnetization axis from the demagnetized state to the saturation state.

It may be true that Eq. (2) applies strictly to a uniaxial magnet, and as our sample was prepared in polycrystalline form, it is not possible to determine whether it has a uniaxial magnetic property, though $CoCr_2S_4$ which is somewhat similar to our sample has been found to have a uniaxial property.[10] In any case, the two-state model should give at least a semiquantitative explanation of the origin of the line broadening of the Mössbauer spectra.

Since the anisotropy energy K in Eq. (2) is expected to be proportional to the work W in Fig. 3, Eq. (2) may be written in the form $f = f_0 \exp(-CW/T)$, where C is a proportionality constant. Using the relatively accurate data for $T = 239$ and 232 K corresponding to the larger line broadening, we calculated f_0 and C to be 0.12×10^9 s^{-1} and 0.050 cm^3 K/ergs, respectively.

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