Orbital dilution effect in Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$

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**Introduction**

When the electronic orbital levels of transition-metal ions are degenerate, the cooperative Jahn–Teller effect generally causes the crystal distortion [1]. Many studies have been performed on spinel-type transition-metal oxides, in which the crystal structure is cubic at high temperatures. For example, in an inverse spinel CuFe$_2$O$_4$, the Jahn–Teller distortion relevant to the $d_{xy}$ orbitals of Cu$^{2+}$ ions at octahedral sites causes a structural transition from cubic to tetragonal at around 630 K [2]. A similar tetragonal distortion is observed in Mn$_2$O$_3$ with Jahn–Teller-active Mn$^{2+}$ ions at octahedral sites. In these compounds, the twofold $d_{xy}$ level of Cu$^{2+}$ and Mn$^{2+}$ is split with the elongated tetragonal distortion. Őpik and Pryce pointed out that the elongated character should result from the anharmonic terms of the elastic energy [3]. FeCr$_2$O$_4$ is another typical cooperative Jahn–Teller system with the spinel structure. Fe$^{2+}$ ions with the high-spin 3$d^6$ configuration selectively occupy tetrahedral sites. One electron of the minority spin therefore occupies the lower-lying twofold $d_{xy}$ level. The orbital degree of freedom of the electron causes cooperative Jahn–Teller distortion below 135 K [4]. The compressed tetragonal character $(c/a)$ of the low-temperature phase is also attributable to the lattice anharmonicity [3].

We have studied the effect of orbital dilution in the spinel-type Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$ system. The substitution of Mn for Fe is regarded as the introduction of voids in terms of orbital degree of freedom, because the high-spin Mn$^{2+}$ ion has no minority-spin electron. In contrast, the spin sector is expected to be less affected by the substitution, because of a rather small difference in the formal magnetic moment between Fe$^{2+}$ and Mn$^{2+}$. In fact, similar successive magnetic transitions have been reported for FeCr$_2$O$_4$ and MnCr$_2$O$_4$ [5-7]. Present investigation in the solid solution shows that the orbital dilution not only reduces the structural transition temperature but also affects the type of cooperative Jahn–Teller distortion. The observed change in distortion type can be explained in terms of a competition between the lattice anharmonicity and the spin–orbit coupling.

**Experimental**

Polycrystalline Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$ samples were prepared by solid state reaction. Magnetization measurements were carried out by using a superconducting quantum interference device. High-resolution x-ray diffraction patterns were collected by using diffractometers on beamlines 4C and 1A.

**Results and Discussions**

Temperature dependence of the x-ray diffraction profile for $x = 0.1$, 0.7, 0.8, and 0.9 is shown in Fig. 1. The structural transition temperature and the peak splitting are clearly suppressed as $x$ increases. In Fe$_{0.9}$Mn$_{0.1}$Cr$_2$O$_4$, the (800) peak begins splitting at around $T_d \sim 130$ K, indicating the cooperative Jahn–Teller distortion related to a ferroic arrangement of occupied $d_{xy}$ orbitals of Fe$^{2+}$. $T_d$ for $x = 0.7$ and 0.8 are approximately 50 K and 40 K, respectively. The lower-angle peak in the $x=0.1$ sample shows a further small split at $T_d \sim 70$ K, indicating another structural transition from tetragonal to orthorhombic. In Fe$_{0.3}$Mn$_{0.7}$Cr$_2$O$_4$, which exhibits a cubic-to-tetragonal transition at a lower temperature than the ferrimagnetic transition temperature, tetragonal distortion of an elongated type $(a<c)$ is observed. The low-temperature orthorhombic phase is absent for 0.7 and 0.8. For $x=0.9$, one does not see splitting of the (800) peak.

The phase diagram of Fe$_x$Mn$_{1-x}$Cr$_2$O$_4$ is summarized in Fig. 2. The cubic-to-tetragonal structural transition temperature $T_d$ decreases as the Mn concentration increases. Here it is interesting to compare the observed orbital dilution effect with the well-known spin-dilution effect in a ferromagnet. A Monte Carlo calculation showed that the site-percolation limit for the diamond lattice is approximately 0.43 [14]. Although Fe$^{2+}$ and Mn$^{2+}$ ions form the diamond lattice in the spinel-type Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$, the phase diagram for Fe$_x$Mn$_{1-x}$Cr$_2$O$_4$ is qualitatively different from that for Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$.
Mn$_{x}$Cr$_2$O$_4$, the cubic-tetragonal transition survives for the orbital concentration at least down to 1-x=0.2, which is much smaller than the percolation limit. $T_s$ is roughly proportional to the Fe concentration 1-x, in accordance with the mean-field theory. This implies the long-range coupling between Fe$^{2+}$ dy orbitals via a strain field in the spinel system, where FeO$_4$ tetrahedra are isolated from one another [5, 15].

The ferrimagnetic transition temperature $T_{N1}$ and the conical magnetic transition temperature $T_{N2}$ are less sensitive to the Mn substitution than the structural transition temperature $T_s$. As a result, $T_s$ decreases to meet the ferrimagnetic transition temperature $T_{N1}$ at around x ~ 0.5. Figure 2 also suggests a strong coupling between magnetism and structure. It seems that the ferrimagnetic transition accompanies a structural transition for x<0.5. The crystal structure transforms to orthorhombic at $T_s$ ~ $T_{N1}$. A similar orthorhombic distortion was reported in some spinel-type mixed chromites, Cu$_{1-x}$Ni$_x$Cr$_2$O$_4$ and Fe$_{1-x}$Ni$_x$Cr$_2$O$_4$ [5]. Pure NiCr$_2$O$_4$ becomes tetragonal with c>a in contrast to CuCr$_2$O$_4$ and FeCr$_2$O$_4$ with the spontaneous tetragonal distortion with c< a. The orthorhombic distortion in the mixed crystals should originate from the competition between the two types of distortion. In the case of Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$ in contrast, MnCr$_2$O$_4$ does not contain any Jahn-Teller-active ions. Therefore, the origin of the orthorhombic distortion should be different from that in Cu$_{1-x}$Ni$_x$Cr$_2$O$_4$ and Fe$_{1-x}$Ni$_x$Cr$_2$O$_4$. The orthorhombic distortion in Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$ should be ascribed to the interplay between spin and orbital at the Fe$^{2+}$ ions. A simple perturbation calculation suggests that the Fe$^{2+}$ minority-spin electron distribution tends to extend perpendicular to the spin moments. The possible orbital shape is attached to Fig. 2.

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References


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Fig. 2: Structural and magnetic phase diagram of Fe$_{1-x}$Mn$_x$Cr$_2$O$_4$.