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Jahn-Teller Distortion in Magnetic Spinels

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Tetragonal distortion of magnetic spinels, especially its temperature dependence is discussed. The distortion is explained theoretically as the Jahn-Teller effect in the crystal. Some theories suggest that the transition should be of the first kind.

Temperature dependences of the distortion of some magnetic spinels are experimentally studied in detail, and it is concluded that the transition is of the first kind.

The compound $CuMn_2O_4$ which contains both manganese and copper exhibits no tetragonal distortion. This is thought to be a compensation effect of cupric and manganic ions. When copper is replaced by zinc or manganese by chromium, the distortion reappears.

The tetragonal distortion in spinel or other cubic crystals which contain cupric (Cu^{++}) or manganic (Mn^{+++}) ions has been studied by many workers[1-9], and the following important facts were experimentally confirmed:

1) The cupric or manganic ion at the octahedral site distorts the crystal so that the axial ratio, $c/a>1$ and the cupric ion at the tetrahedral site distorts the crystal so that $c/a<1$.
2) There exists a critical concentration of the cupric or manganic ion above which the distortion occurs.
3) The distortion disappears above a critical temperature.

Sinha *et al.*[2] explained the distortion as caused by the cooperative alignment of the distorted octahedra. Dunitz and Orgel[3] explained the distortion of an octahedron as the Jahn-Teller effect in the crystal, that is, the orbital state of the central magnetic ion which is degenerate in the cubic field has its degeneracy removed by distorting the octahedron of surrounding anions. Goodenough[4] explained it in a somewhat different way. Wojtowicz[5] improved Sinha's theory and concluded that the tetragonal-cubic transition must be of the first kind, and the tetragonality, c/a-1, jumps at the transition point by one half of a whole change. In his theory, this jump is attributed purely to statistical nature. Kanamori[6] explained the distortion from a fundamental Hamiltonian, where the interaction between the lattice vibration and electron cloud is taken into account. If one neglects the anharmonic vibration and the higher order interaction, the anisotropy in energy concerning the strain components does not come out and the second kind transition is obtained. If one takes those terms into account, the first kind transition is expected.

Recently, many experimental studies are carried out in our country. Among these some results are worthwhile to cite briefly.

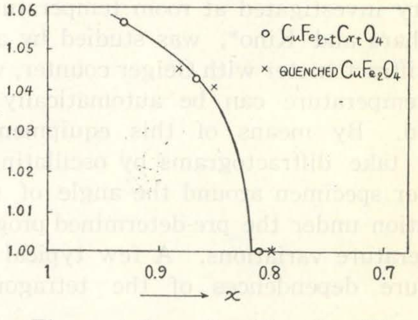

Fig. 1. The variation of axial ratio with cation distribution parameter for iron rich copper ferrite-chromite and quenched copper ferrite.

Ohnishi and Teranishi[7] studied the copper ferrite-chromite system, in which one can control the concentration of cupric ions in the octahedral site either by mixing chromite or by thermal treatment of pure copper ferrite. The distortion, however, depends merely upon the copper concentration and never how to control it. They found that there exists a critical value in the concentration of cupric ions that causes the distortion, which is found to be 40%. Miyahara and Muramori[8] studied the magnesium manganite-ferrite system and determined the critical concentration of manganese ion to be 60%, which agrees well with the results recently obtained by Irani[9], Sinha and Biswas in the manganite-aluminate system independently. In their study, however, no jump of the distortion is found in the temperature dependence. This accords with Sinha's theory but contradicts Wojtowicz's and experimental results obtained by our colleagues.

The main problem, which will be dealt with here, is the temperature dependence of of the distortion. Ohnishi and Teranishi have already studied the temperature dependence of the transition in the copper ferrite-chromite system by means of a high temperature X-ray camera and concluded that the transition might be of the first kind, and the results were compared with theories by Wojtowicz and Kanamori.

The experiment is, however, not detailed enough to determine the character of the transition or to compare with Kanamori's theory which accounts for the jump at the transition point.

In order to clarify this problem, the system of copper ferrite-aluminate, which was preliminary investigated at room temperature by Miyahara and Kino*, was studied by an X-ray diffractometer with Geiger counter, where the temperature can be automatically controlled. By means of this equipment we could take diffractograms by oscillating the powder specimen around the angle of (311)-reflection under the pre-determined programs temperature variations. A few typical temperature dependences of the tetragonality are shown in Fig. 2, where steep decreases of the distortion near critical temperature are seen. The temperature dependence in nickel chromite studied recently by T. Tsushima, shows a quite similar feature of the curve to that of copper ferrite apart from low transition temperature. From these experiments we are inclined to conclude that the transition is of the first kind. Another evidence of the first kind transition is that two phases, tetragonal and cubic, appear near the transition point. In Fig. 4 the diffractograms of (311) reflections of a copper ferrite-aluminate are shown. In lower temperatures (113) and (311) lines are separated, and in higher temperatures these lines coincide with each other, showing the cubic structure, and in intermediate temperatures it is clearly seen that both tetragonal and cubic phases are co-existing.

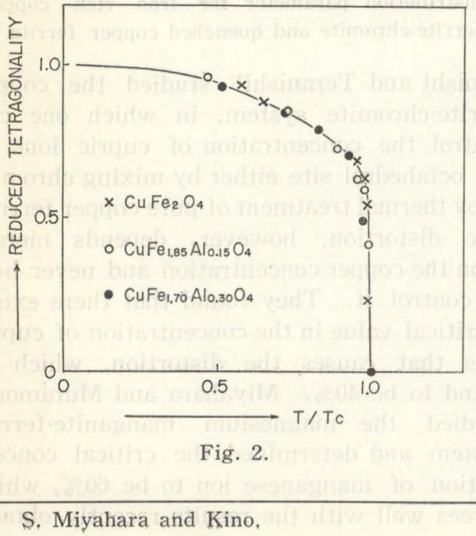

Fig. 2.

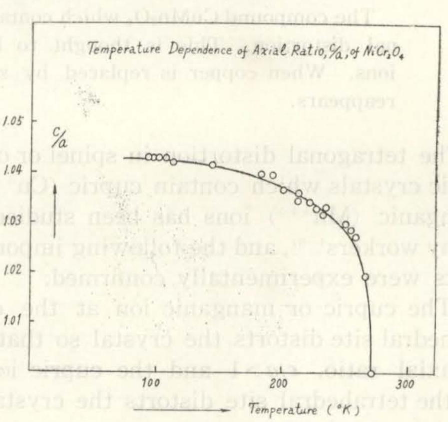

Fig. 3,

Two phases are more obviously seen in the case of mixed manganese compounds such as copper manganite-chromite, magnesium manganite-ferrite[8], copper-zinc manganite*, and hausmannite-cobalt manganite**.

All of the three theories by Sinha, Wojtowicz and Kanamori do not take the migration of ions into account. The transition point corresponds to the temperature where free energy of the cubic phase becomes equal to that of the tetragonal phase under the same ionic arrangement. If ions can migrate, the crystal separates into two phases; one is more and the other is less in manganese content, and the manganese-rich phase might

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* S. Miyahara and Kino.

* Y. Aiyama.

** I. Aoki, not published.

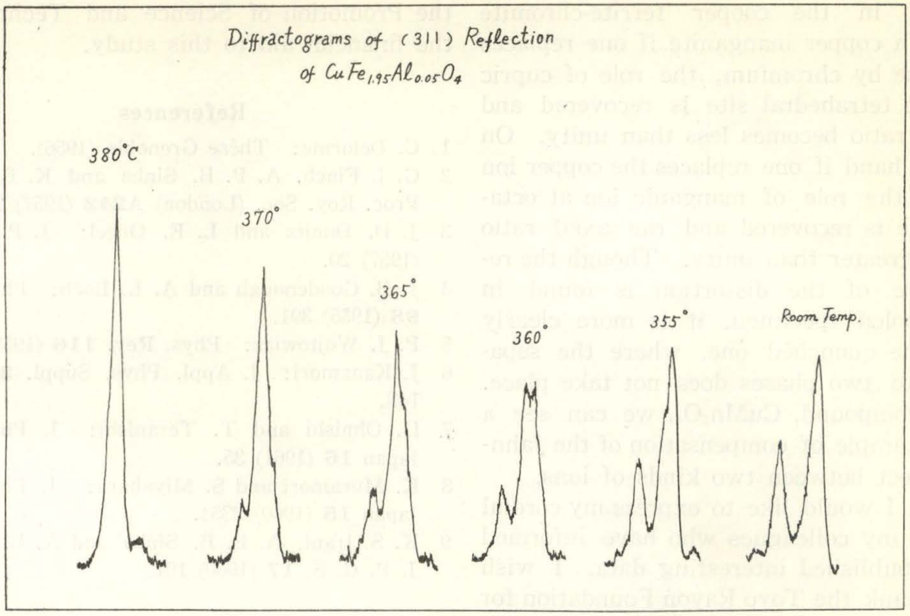

Fig. 4.

lower its free energy by taking the tetragonal structure and the manganese-less phase does so by taking the cubic structure. This situation is almost same as the case of ordinary two phases which appear in two component alloys. But, the difference consists in the energy. In the case considered here, the energy is thought to be the interaction between orbital motion of the electrons in the ion and the lattice vibration. In the case of manganese compounds this energy would be high, corresponding to large distortion and high transition temperature. At higher temperatures the ions have considerable mobility and a separation of two phases might occur. On the other hand, in the case of copper ferrite the energy is less, corresponding to less tetragonality and lower transition temperature, so that the ions do not move so freely as in the case of manganese compound. Thus, in the copper ferrite-chromite or in copper ferrite-aluminate system we can observe two phases only in a narrow region.

In addition, copper manganite $CuMn_2O_4$ and its mixed compounds exhibit an interesting property. Pure copper manganite is cubic even at low temperatures. This fact is plausibly explained by considering that the two opposite tendencies, one to make $c/a<1$ caused by the cupric ion on tetrahedral site and the other to make $c/a>1$ caused by manganic ion on octahedral site, are compensated with each other and the crystal remains cubic. A similar compensation between ions of the same kind is already found by Ohnishi and

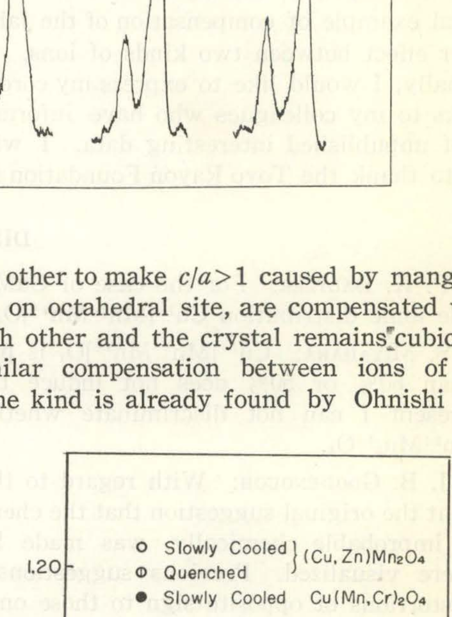

Fig. 5.

Teranishi in the cooper ferrite-chromite system. In copper manganite if one replaces manganese by chromium, the role of cupric ion at the tetrahedral site is recovered and the axial ratio becomes less than unity. On the other hand if one replaces the copper ion by zinc, the role of manganic ion at octahedral site is recovered and the axial ratio becomes greater than unity. Though the reappearance of the distortion is found in slowly cooled specimen, it is more clearly seen in the quenched one, where the separation into two phases does not take place. In this compound, $CuMn_2O_4$, we can see a typical example of compensation of the Jahn-Teller effect between two kinds of ions.

Finally, I would like to express my cordial thanks to my colleagues who have informed me of unpublished interesting data. I wish also to thank the Toyo Rayon Foundation for the Promotion of Science and Technics for the financial aid to this study.

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DISCUSSION

P. K. BALTZER: For the case of $CuMn_2O_4$, have you considered the possibility of the ionic distribution $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$, which also can explain the cubic structure?

S. MIYAHARA: $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$ is possible. Since it is known that Mn^{3+} ion less than 60% or 50% does not induce the distortion, it may remain to be cubic. At present I can not discriminate whether the valence state is $Cu^{1+}Mn^{3+}Mn^{4+}O_4$ or $Cu^{2+}Mn_2^{3+}O_4$.

J. B. GOODENOUGH: With regard to the compound $CuMn_2O_4$, it might be pointed out that the original suggestion that the chemical formula could be $Cu^{+}[Mn^{3+}Mn^{4+}]O_4$, which is improbable chemically, was made because only static Jahn-Teller stabilizations were visualized. Previous suggestions that A-site Jahn-Teller ions which stabilize distortions of opposite sign to those on the B-sites, tend to compensate statically to give cubic symmetry seem highly improbable. However, considerable Jahn-Teller stabilization can be achieved dynamically, the electron configuration adjusting to the instantaneous configuration of the neighboring ligands. It is possible that static Jahn-Teller effects give way to dynamic effects when competing Jahn-Teller ions occupy the different types of lattice site.

E. BANKS: We have observed what appears to be a similar effect in ferrites where Cu^{2+} is substituted for Fe^{3+}, with compensation by fluorine ion. A sample of composition $Cu_{1.5}Fe_{1.5}O_{3.5}F_{0.5}$, prepared under conditions of very slow cooling, turns out to have a cubic spinel structure, which may be the result of opposing Jahn-Teller distortions for Cu^{2+} on A and B sites.