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METALLIC ANTIFERROMAGNETISM OF \((V_{1-x}Ti_x)O_3\) \((0.06 \leq x \leq 0.30)\)

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Résumé.- L'étude par effet Mössbauer de \((V_{1-x}Ti_x)O_3\) dopé en \(^{57}\)Fe \((x \geq 0.06)\) qui est métallique jusqu'au zéro absolu, confirme que le système est antiferromagnétique.

Abstract.- Mössbauer effect measurement of \(^{57}\)Fe doped in \((V_{1-x}Ti_x)O_3\) \((x \geq 0.06)\), which shows a metallic conductivity down to absolute zero, confirmed the metallic antiferromagnetism of the system.

\(V_2O_3\) shows a high temperature metal (M(P)) to low temperature insulator (I(AF)) transition at about 170 K \((T_c)\), accompanying with the structural change from hexagonal to monoclinic structure. Shinjo and Kosuge confirmed for the first time by means of the Mössbauer effect measurements of \(^{57}\)Fe doped in \(V_2O_3\) /1/ that the insulating phase is antiferromagnetic. In the metallic phase, the magnetic susceptibility \((\chi)\) vs. temperature \((T)\) curve obeys the Curie-Weiss law. It has been an interesting problem whether the metallic phase orders magnetically at low temperature. Unfortunately, the first order transition happens to stoichiometric \(V_2O_3\) at \(T_c\). It is well known that the substitution of Ti for V, excess oxygen and high pressure stabilize the metallic phase of \(V_2O_3\) down to lowest temperature /2,3,4/. Our recent studies on the nonstoichiometric \(V_2O_3+x\) system \((0 < x < 0.08)\) /5/ showed that the stabilized magnetic phase \((x \geq 0.04)\) orders antiferromagnetically at about 10 K. Recently, Dumas et al. suggested by the magnetic susceptibility measurement /6/ that the metallic \((V_{1-x}Ti_x)O_3\) \((x \geq 0.06)\) also orders antiferromagnetically at lower temperature.

This paper treats the magnetism of \((V_{1-x}Ti_x)O_3\) studied by the Mössbauer effect of \(^{57}\)Fe doped in the sample.

The samples \((V_{1-x}Ti_x)O_3\) \((0 < x < 0.3)\) were prepared by arc melting of an appropriate mixture of \(V_2O_3\), Ti metal and TiO\(_2\). For the Mössbauer measurements, the samples of \((V_{1-x}Ti_x)O_3\) \((x = 0.04, 0.10, 0.16)\) including 1.5 mole \% \(^{57}\)FeO\(_2\) were prepared by the ceramic or arc melting method. All the samples have the corundum structure at room temperature. Susceptibility curves of \(^{57}\)Fe doped samples showed that the effect of impurity Fe on the intrinsic properties of \((V_{1-x}Ti_x)O_3\) is not so significant. The Mössbauer measurements were made at 4.2, 77 K and room temperature. The velocity scale in Mössbauer spectra was calibrated with pure Fe metal or \(\alpha\)-Fe\(_2\)O\(_3\).

The magnetic susceptibility measurements show that \(T_c\) decreases with increasing \(x\) and disappears around at \(x = 0.05\). For \(x \geq 0.06\), \(\chi\) vs. \(T\) curves show another kind of anomaly at a temperature \((T_N)\), which increases with increasing \(x\). The Mössbauer spectra at room temperature show that all samples are paramagnetic. At 4.2 K, each sample shows magnetic hyperfine splitting, and the hyperfine field is about 390 kOe for the sample with \(x = 0.04\) (insulating) and about 320 kOe for the samples with \(x = 0.10\) and 0.16.

Typical spectra are shown in the inset of figure 1. From the structure and the temperature dependence of the spectra, there is no doubt that the magnetic hyperfine field is due to a long-range magnetic ordering and not due to slow relaxation of a paramagnetic ion. Therefore it is apparent that the anomaly of \(\chi\) vs. \(T\) curves for the samples with \(x \geq 0.06\) is caused by the antiferromagnetic ordering. A phase diagram obtained from above-mentioned experimental results is shown in figure 1. This is in good agreement with the data of McWhan et al. /2/ except for the existence of the antiferromagnetic metallic (M(AF)) phase. The change of \(T_N\) is also in good agreement with the data of Dumas et al. /6/.

Both excess oxygen and substitution of Ti stabilize the metallic phase of \(V_2O_3\) and the metallic phase shows the paramagnetic to antiferromagnetic transition in either case. The hyperfine field of Fe in M(AF) phase is about 320 kOe for \((V_{1-x}Ti_x)O_3\) system and about 280 kOe /5/ for \(V_2O_3+x\) system, and is smaller than that (about 460 kOe) /7/ of Fe in I(AF) phase of stoichiometric \(V_2O_3\). This reflects the metallic properties of the matrix i.e. a consi-
derable fraction of the 3d electrons of Fe atom participates in the metallic bonding, thus reducing the magnetic moment much below 5 μ_B.

In I(AF) phase of the (V_{1-x}Ti_x)2O_3 (x < 0.04), the hyperfine field (390 kOe) of Fe is smaller than that in V_2O_3, and that (460 kOe for x = 0.02) /5/ in the V_{2}O_{4+x} system is the same as that in V_2O_3. As pointed out by Wertheim et al. /7/, impurity Fe in V_2O_3 acts as an acceptor (localized state), and it shows a hyperfine field of 460 kOe at 4.2 K. Thus we can conclude safely that Fe in V_{2}O_{4+x} is in impurity level and exists as a trivalent ion. On the other hand, we feel that Fe in (V_{1-x}Ti_x)2O_3 is in delocalized state (band filling electron) and so the hyperfine field of Fe becomes smaller than that of a trivalent iron.

Present measurements confirmed that in not only V_{2}O_{4+x} system but also (V_{1-x}Ti_x)2O_3 system, the metallic phase orders antiferromagnetically at low temperature. From these experimental results, we believe that the antiferromagnetic metallic phase is intrinsic in the stoichiometric V_2O_3.

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References