MÖSSBAUER STUDIES ON DILUTE Tc-(Fe) ALLOYS

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Résumé.- L'effet quadrupolaire et le déplacement isomérique (par rapport au Fe- α) d'un alliage dilué Tc-Fe sont égaux à -0.13 ± 0.02 mm/s et -0.020 ± 0.006 mm/s respectivement. Des mesures de champ hyperfin en champ extérieur de 30 à 50 kOe pour $1.5 < T < 4.2$ K montrent que le champ à saturation est de -7.4 ± 1 kOe pour une susceptibilité locale de -0.145 ± 0.009 . Ces résultats et une étude précédente sur la supraconductivité des alliages Tc-Fe indiquent l'existence de fluctuations de spin localisées dans ce système.

Abstract.- The quadrupole splitting and the isomer shift of a dilute Tc-Fe alloy have been determined as -0.13 ± 0.02 mm/s and -0.020 ± 0.006 mm/s (relative to α -Fe), respectively. The hyperfine field measurement in the external magnetic field of 30 and 50 kOe for $1.5 < T < 4.2$ K shows that the saturation field for 50 kOe is -7.4 ± 1 kOe and the local susceptibility is -0.145 ± 0.009 . These results and the previous study on the superconductivity of Tc-Fe alloy indicate the existence of localized spin fluctuation in this system.

In our recent paper /1/ the Mössbauer effect measurement of a dilute ^{57}Fe impurity in Tc was reported for the first time, where the quadrupole splitting (QS) and the isomer shift (IS) were determined. The hyperfine field measurements indicate that the magnetic character of Fe impurities in Tc lies in the intermediate region between non magnetic to magnetic. For further information on the magnetic behavior of a dilute Tc-Fe alloy, the experiment of hyperfine fields was performed with a newly prepared sample.

A source of ^{57}Co incorporated in Tc was prepared by means of electrodeposition and reduction. The carrier free ^{57}Co (CoCl_2) and Tc (NH_4TcO_4) were simultaneously electroplated on a Tc film previously electroplated on a Cu substrate. The sample was then reduced in a highly purified hydrogen atmosphere for 46 h at 900°C . The radioactive intensity of ^{57}Co was 35 μCi , corresponding to 0.5 ppm of the host Tc. The concentration of cobalt is extremely small in terms of the optimum Mössbauer condition, but for such a small concentration the effect of interactions between Fe impurities can be neglected. An X-ray diffraction study confirmed the hcp structure of metallic Tc ($a = 2.74 \text{ \AA}$, $c = 4.40 \text{ \AA}$) and revealed that the c -axis is preferentially oriented perpendicular to the surface.

It is well known that in hcp transition metals there is an electric field gradient (EFG), resulting in appearance of a QS /2/. Determinations of the QS and the IS were performed as followings : The spectra in zero magnetic field at room tempera-

ture were observed with an absorber of potassium ferrocyanide for two source orientations, $\theta = 0^\circ$ and 60° , where θ is the angle between the γ -ray direction and the c -axis texture of the sample. Both spectra appeared as a broad single line. On the assumption that the spectrum consists of two lines, the computer analysis was carried out, where QS, IS and line width in these spectra were simultaneously fitted. The ratios of line intensities are 1:1.4 and 1:1.1 for $\theta = 0^\circ$ and 60° , respectively. This means that the sign of the EFG is negative, taking into consideration the texture of the sample. Thus the QS is determined as -0.13 ± 0.02 mm/s and the IS relative to α -Fe is -0.020 ± 0.006 mm/s, where the negative sign signifies a larger electron density at the nuclei. These values are in good agreement with our previous results /1/ found by using a nichrome film as a substrate.

The hyperfine fields (H_{hf}) were measured in the external fields (H_{ext}) of 30 and 50 kOe for $1.5 < T < 4.2$ K, where the superconducting state was quenched. The spectra were analyzed by assuming the Lorentzian lineshape and the ideal intensity ratio of 3:0:1:1:0:3. The effective field ($H_{eff} = H_{ext} + H_{hf}$) at an Fe nucleus was determined from the splitting width between outer two lines. In figure 1 is shown H_{hf} versus H_{ext}/T for $H_{ext} = 30$ and 50 kOe. The numerical values of H_{hf} are : -4.3 kOe ($H_{ext} = 30$ kOe, $T = 2.50$ K), -4.5 kOe (30 kOe, 4.22 K), -7.2 kOe (50 kOe, 1.52 K), -7.5 kOe (50 kOe, 2.50 K), -6.8 kOe (50 kOe, 4.22 K). These values are consistent with our previous results /1/ within experi-

mental error.

Fig. 1 : ^{57}Fe hyperfine field H_{hf} versus H_{ext}/T for a dilute Tc-Fe alloy, where the external field H_{ext} is 30 and 50 kOe, and temperature is $1.5 < T < 4.2$ K.

From the figure, the saturation field seems to depend on H_{ext} , but the local susceptibility H_{hf}/H_{ext} is independent of H_{ext} for $1.5 < T < 4.2$ K, $H_{hf}/H_{ext} = -0.145 \pm 0.009$. Although H_{hf} includes the Van Vleck contribution (H_v) from excited electronic states which is proportional to H_{ext} , the term H_v is usually positive and is only a few percent of H_{ext} (for example 3 % for Mo-Fe /3/ and 1 % for Nb-Fe /4/ both 4d hosts). In the present case, H_v was not measured, but may be ignored within experimental error. Thus the observed small negative H_{hf} can be attributed to the local magnetization of Fe impurities. The saturation field of -7.4 ± 1 kOe for $H_{ext} = 50$ kOe is much smaller than those for the case where an Fe impurity has a well defined magnetic moment, even for the case where the Kondo effect exists. Our result is consistent with the macroscopic susceptibility measurement of Tc-3.73 at.% Fe, which has proved that the susceptibility is independent of the temperature above 50 K /5/. These results indicate that an Fe impurity in Tc has no well defined magnetic moment.

It is interesting to note that the present hyperfine fields resemble the behavior of those found in the Ir-Fe alloy /6/ which is the well established localized spin fluctuation (LSF) system. In this case the maximum H_{hf} is -11.7 kOe at 62 kOe and 1 K, and $(H_{hf} - H_v)/H_{ext}$ is -0.126 ± 0.005 for $30 < H_{ext} < 62$ kOe and $1 < T < 7$ K. In addition, our recent studies of the effect of Fe impurities on the superconductivity of Tc indicate the existence of LSF in this system. Experimental evidence and

above discussion lead us to the conclusion that the small hyperfine field is attributed to the LSF.

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