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Mössbauer Spectroscopy of ^{57}Fe Impurities in Technetium

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The Mössbauer effect of a dilute ^{57}Fe impurity in Tc was measured for the first time. The isomer shift and the quadrupole splitting at room temperature are -0.02 ± 0.01 and -0.13 ± 0.02 mm/s, respectively. Small induced magnetic fields, -4.5 ± 1 and -7.5 ± 1 kOe, were found in external magnetic fields of 30 and 45 kOe at 4.2 K. This indicates that the magnetic character of Fe impurities in Tc lies in the intermediate region between magnetic and nonmagnetic. The induced field may be attributed to local spin fluctuation.

Mössbauer-effect studies for ^{57}Fe as an impurity in transition metals have been done by many workers. For example, Qaim[1] investigated the isomer shift of ^{57}Fe embedded as a dilute impurity in 32 different metallic host lattices. The quadrupole splitting observed with the hexagonal transition metals[2,3] gave valuable information on the electric field gradient (EFG) in these metals. In addition, the Mössbauer effect is very useful to study the formation of the local magnetic mo-

ment associated with the impurity in metals.[4,5] However, to the authors' knowledge, a measurement on ^{57}Fe in Tc has not been reported so far.

Technetium is a 4*d* transition metal for which the number of outer electrons is seven, and has the hcp structure which is expected to give an EFG. Since the magnetic character of the Fe impurity in Tc is expected to be in the transition region from the nonmagnetic to the magnetic state, a measurement under high magnetic fields at low temperature is very interesting for investigations of the formation of a local magnetic moment. In this paper, we report a Mössbauer-effect study of a very dilute ^{57}Fe impurity in Tc.

Preparation of metallic Tc by means of electrodeposition and reduction was previously reported.[6] By similar method, a source of ^{57}Co incorporated in Tc was prepared. For electrodeposition, we used Tc in the chemical form of $NH_4(^{99}Tc)O_4$ in aqueous solution and carrier-free ^{57}Co in dilute HCl solution. These were simultaneously electroplated in H_2SO_4 electrolyte (pH 1.0) on a thin film of iron-free Nichrome (vapor-deposited on a ceramic base). By adding the electrolyte during deposition, the change in ion concentrations of ^{99}Tc and ^{57}Co was minimized. The sample was then reduced in a highly purified hydrogen atmosphere for 4 h at 950°C. The amounts of ^{99}Tc and ^{57}Co in the sample were determined by measuring the activity of the residual solution with a liquid-scintillation counter and with a Ge(Li) detector. The radioactive intensities of the sample thus determined were 70 μCi for ^{99}Tc and 90 μCi for ^{57}Co, corresponding to 4.1 mg of ^{99}Tc and 5 ppm of ^{57}Co. The cobalt concentration in the sample is extremely small in terms of the optimum Mössbauer condition. The 14.4-keV γ-ray count accumulated in a multichannel analyzer was only about 200 counts per hour per channel.

Analysis by a scanning electron microscope showed that the metallic Tc produced is granular having a diameter of 2.1–2.9 μm. The area of this sample is 45 mm^2 and the thickness was estimated to be roughly 15 μm. An x-ray diffraction study confirmed the hcp structure of metallic Tc (a = 2.74 Å, c = 4.40 Å) and revealed the texture of the sample. The c axis is preferentially oriented perpendicular to the surface. Impurity analysis was made by using an x-ray microprobe analyzer. Diffusion of the basic Nichrome into Tc was not above the threshold for detection, 100 ppm for Ni. A similar study with a sample containing nonactive Co at a concentration of 0.17 at.% showed no appreciable maldistribution of Co in the sample.

For further confirmation of the production of metallic Tc by the present method, the superconducting transition temperature of the sample was measured by both resistive and inductive methods, and was determined to be 7.45 ± 0.05 K. This value is slightly smaller than that of a sample prepared by the ion-sputtering method, 7.70 K.[7] The upper critical magnetic field of the superconducting state was also measured in the temperature range of 1.3–8 K, and we found that an external magnetic field of 25 kOe is sufficient to destroy the superconducting state of our sample at 4.2 K. Details of our study on the superconducting properties will appear elsewhere.

The Mössbauer spectra were obtained by the usual method, where the source was at room temperature and at 4.2 K, whereas the absorber was always kept at room temperature. The absorbers used were, respectively, $K_4[Fe(CN)_6]3H_2O$ containing 0.5 mg/cm^2 of ^{57}Fe and stainless steel containing 1.0 mg/cm^2 of ^{57}Fe. Calibrations of velocity and isomer shift were made by the known magnetic splitting of ^{57}Fe contained in natural iron.

As shown in Fig. 1, the spectrum observed in zero magnetic field at room temperature is a single broad line. The full width at half-maximum was found to be larger than that for ^{57}Co in Cu

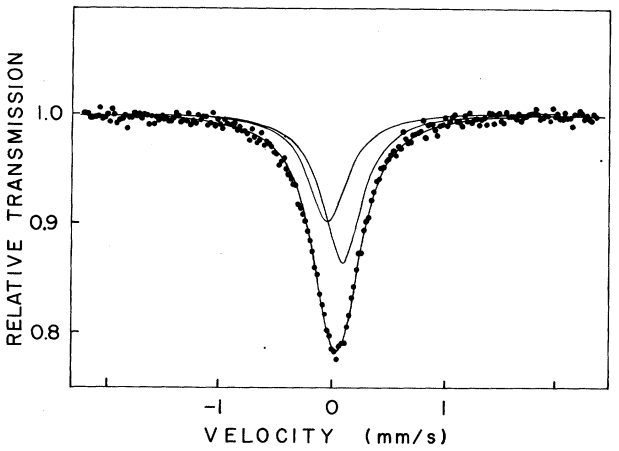

FIG. 1. Mössbauer spectrum of a ^{57}Co in Tc source measured in zero magnetic field at room temperature. The absorber is $K_4[Fe(CN)_6]3H_2O$ containing 0.5 mg/cm^2 of ^{57}Fe. Solid lines express the best computer fits. The quadrupole splitting occurring in the Tc source is seen in the structure of the resonance line. The velocity scale is relative to α-Fe and negative velocity means that the absorber is moving toward the source.

by 0.11 mm/s. This broadening suggests the existence of quadrupole splitting which is well known for hcp transition metals. A computer analysis, made on the assumption that the spectrum consists of two lines, exhibits the ratio of line intensities, 1:1.4. This indicates that the sign of the EFG is negative, taking into consideration the texture of the present sample, i.e., the EFG axis is mainly parallel to the 14.4-keV γ rays. Thus the quadrupole splitting was determined to be -0.13 ± 0.02 mm/s. This value is reasonable compared to other hcp transition metals, and is similar to the value for Ru, -0.14 mm/s.[3]

The isomer shift relative to α-Fe is -0.02 ± 0.01 mm/s (center of the doublet in Fig. 1). The negative sign signifies a larger electron density at the nuclei. This value is somewhat smaller than those found with other 4*d* hosts. However, in the case of 3*d* and 5*d* hosts, the isomer shifts for Mn and Re, both of which have seven outer electrons, are also smaller than those of other hosts in the same series.[8] This means that the electron density at Fe nuclei is maximum for the host metals with seven outer electrons. The spectrum observed at 4.2 K also has a single line and the isomer shift is $+0.08 \pm 0.01$ mm/s.

Clogston *et al.*[9] showed from susceptibility measurements that the magnetic character of Fe impurities changes from magnetic to nonmagnetic when the host changes from Mo to 5*d* Re. In order to find the magnetic character of the dilute Fe impurity in Tc, we performed Mössbauer measurements in external magnetic fields (30 and 45 kOe). In Fig. 2 is shown the spectrum at 45 kOe and 4.2 K. Analysis was made on the assumption that both the magnetic field and the EFG axis are perfectly parallel to the γ-ray direction, resulting in an intensity ratio of 3:1:1:3. This assumption is good enough to estimate the effective magnetic field because of the small quadrupole interaction. The effective field thus obtained is 37.5 ± 1 kOe, from which the induced magnetic field is determined to be -7.5 ± 1 kOe. The shift of the inner lines toward negative velocity is consistent with the negative sign of the EFG. For an external magnetic field of 30 kOe, the induced magnetic field is -4.5 ± 1 kOe. These small magnitudes of the induced field prove that Co clusters do not exist in the sample.

It is of interest to compare our results with two typical cases. (1) An Fe impurity in Mo has a definite magnetic moment and shows an induced field of -96 kOe for an applied magnetic field of 62 kOe at 4 K.[10] At a very low temperature, less than 1 K, the situation is more complicated because of the Kondo effect. (2) An Fe impurity in Nb has no magnetic moment and the hyperfine field is less than 1 kOe.[4]

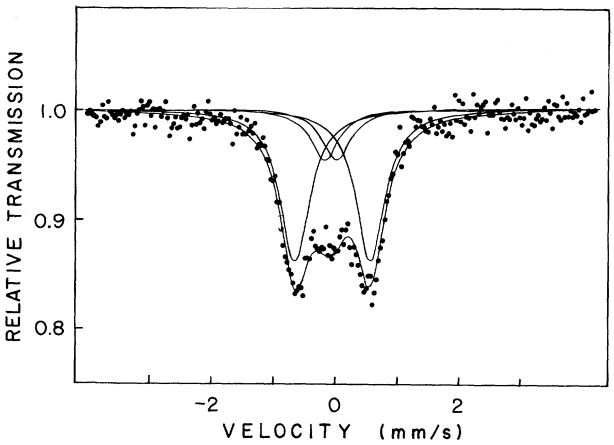

FIG. 2. Mössbauer spectrum of a ^{57}Co in Tc source measured in a 45-kOe magnetic field at 4.2 K. The absorber is stainless steel containing 1.0 mg/cm^2 of ^{57}Fe. Computer analysis was made on the assumption that both the magnetic field and the EFG axis are perfectly parallel to the γ-ray direction.

An Fe impurity in Tc is in the intermediate region between the above two cases. In the 5*d* series, the critical region occurs just at or to the right of Ir.[11] A study on ^{57}Fe in Ir exhibited an internal field induced at 45 kOe and 4.2 K of -8.6 kOe, and the maximum value is -11.7 kOe at 62 kOe and 1 K.[12] Our results are quite comparable to those for the Ir case, but are much smaller than those for the cases where a definite localized magnetic moment is observed. In the case of Ir, the characteristic temperature dependence of the susceptibility and of the resistivity is explained as the effect of localized spin fluctuation.[13,14]

Experimental evidence and the above discussion lead us to the conclusion that the magnetic character of a dilute Fe impurity in Tc lies in the transition region from the nonmagnetic to the magnetic state and that the small induced magnetic field may be due to local spin fluctuation. To obtain further information on the magnetic behavior of dilute Fe impurities in Tc, studies on the external-field dependence as well as the temperature dependence of the hyperfine field are in progress.

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