

Mössbauer effect investigations of FeZn alloy and analysis using charge shift model

H C VERMA

Department of Physics, Patna Science College, Patna University, Patna 800 005, India

MS received 29 June 1983; revised 29 November 1983

Abstract. Mössbauer studies of metallurgically prepared FeZn alloy reveal that it undergoes an irreversible phase change on heating. The new phase starts precipitating at temperatures below 403 K and causes an apparent decrease in quadrupole splitting. The results are analysed in the framework of charge shift model and it is suggested that the vibrations of iron ion in zinc are likely to be much less anisotropic than those of zinc ions in pure zinc.

Keywords. Mössbauer effect; alloys; electric field gradient; iron-zinc alloy; charge shift model.

1. Introduction

The iron-zinc system forms a number of intermetallic phases and the solid solubility of iron in zinc is small. This presents much difficulty in preparing substitutional alloy of zinc with iron impurity. Mössbauer studies of FeZn system have been reported by various workers (Dunlop *et al* 1978; Housley and Nussbaum 1965; Kundig *et al* 1965; Verma and Rao 1981) with the aim of finding the electric field gradient (EFG) at iron probe and its dependence on temperature. The results are only in approximate agreement and depend on the method used to prepare the sample. Verma and Rao (1981) have reported that substitutional alloy may be prepared by keeping zinc and iron ($\sim 0.1\%$ at.) at 600°C for about 150 hr followed by quenching in water. The EFG at iron probe was measured at 80 K and 298 K and almost equal values were obtained.

We report here the Mössbauer measurements on these samples at temperatures above room temperature. The experiments show that the alloy undergoes irreversible phase change on heating. The changes start below 403 K, are much more clear at 466 K and are retained after cooling.

The EFG in FeZn system is compared with the conduction electron charge shift model (CSM) suggested by Bodenstedt and Perscheid (1978). The comparisons suggest that the vibrations of iron impurity in zinc are likely to be much less anisotropic than the vibrations of zinc in pure metal.

2. Mössbauer studies of FeZn alloy

The sample preparation and other experimental details were described in Verma and Rao (1981). Highly pure (99.999%) zinc and iron enriched in iron-57 to 92% were sealed in quartz tubes and were kept at 600°C for about 150 hr and were then quenched

in water. The resulting shining balls were powdered with diamond files and x-ray diffraction patterns were recorded with copper target. The peak positions as well as the intensities (relative) of various peaks matched very well with the diffraction pattern of pure zinc powder under identical conditions. The absence of extra peaks or humps reveals that no intermetallic compounds are formed in significant amount. The Mössbauer spectra showed reasonably narrow lines indicating that the iron ions occupy unique sites. The other Mössbauer parameters also agreed with the previous studies on substitutional alloys. All this confirmed that we are measuring EFG in a substitutional dilute impurity alloy FeZn. It may be mentioned here that the above procedure of sample preparation was chosen out of several attempts with different heat treatments.

The rolled sample foil was kept inside the vacuum furnace for Mössbauer work. The temperature of the sample could be maintained constant to within 1°C using off/on relay controller. The air pressure inside the furnace was kept at $\sim 10^{-5}$ torr by continuous diffusion pumping. The Mössbauer spectra recorded under identical geometrical conditions at 298, 403, 466 and again at 298 K are shown in figure 1.

Evidentially, the system has changed its structure due to the heat treatment it has received during the experiments at high temperatures. The changes seem to start below 403 K, and are retained after cooling. To have an idea as to how much of the sample has changed its phase, the Mössbauer spectrum of the alloy cooled after high temperature experiments was fitted to a single line superposed on a quadrupole doublet. The parameters of the doublet were fixed at the values obtained with the substitutional alloy (part a of figure 1). The fittings with the separated individual components are shown in part d of figure 1. It may be inferred from these fittings that the new phase is being represented by a single line with centre shift $0.359(6)$ mm/sec with respect to rhodium and the relative contribution of this phase is about 55%. If the spectrum at 403 K is fitted to a sum of two independent Lorentzian curves, separation between the lines is about 10% less than the quadrupole splitting observed at room temperature. This may not be taken as a decrease in EFG as is clear from the spectrum at 466 K which shows that the alloy was in the process of phase change.

It may be mentioned here that Kündig *et al* (1965) reported an 8% decrease of quadrupole splitting in FeZn between 296 K and 373 K, whereas Dunlop *et al* (1978) did not observe any such change upto 400 K. The results of our experiments suggest that the discrepancy may be due to different sample preparation methods and the EFG may be essentially independent of temperature.

3. Comparison with charge shift model

The details of the procedure of calculations are described in Bodenstedt and Perscheid (1978). The model is based on the assumption that the conduction electrons of the HCP metals may be replaced by spherical charge clouds situated midway between the positive ions. The charges on these clouds are obtained from the electrostatic stress developed and the resulting departure of the ratio c/a from ideal value $(8/3)^{1/2}$. Point-wise summation over the lattice for the contributions of positive ions and from negative charge clouds then yields total EFG. Isotropic vibrations of the probe do not play a role in this model, but the anisotropic vibrations contribute to EFG. The temperature dependence of EFG is particularly sensitive to anisotropic probe vibrations.

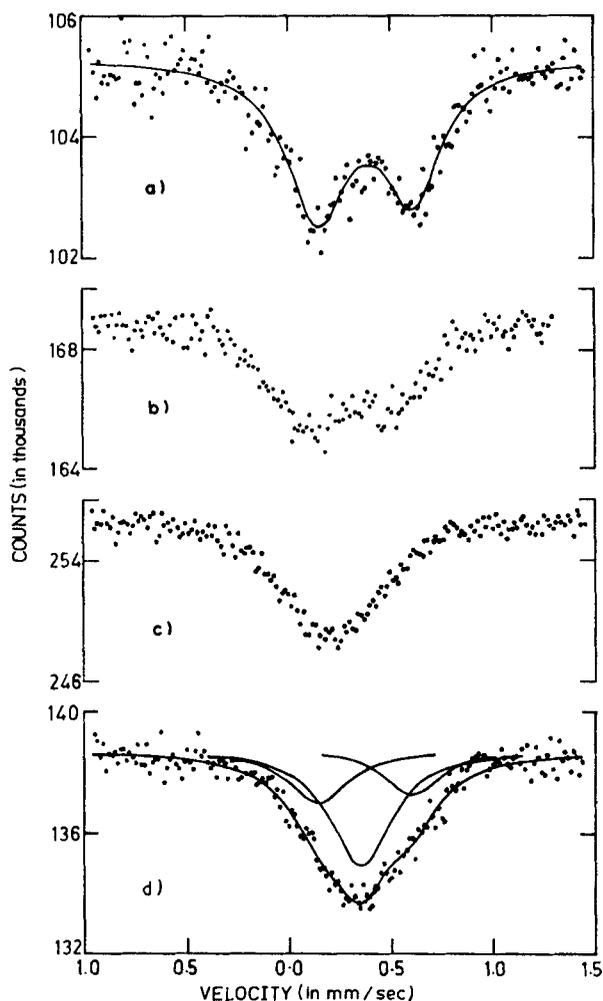


Figure 1. Mössbauer spectra of FeZn at a. 298 K; b. 403 K; c. 466 K and d. 298 K with same sample cooled after high temperature measurements.

The probe dependence of EFG is taken into account by assuming that the difference between effective ionic charges of probe and host changes the charges of nearest neighbour negative clouds. Though it is only a rough approximation, it has successfully described the EFG in a number of systems (Verma and Rao 1981; Maio *et al* 1982). As the conduction electrons may have finite overlap with the ionic charges, there is an uncertainty in the effective values of the charges on ions. The reported values correspond to $Z_{\text{eff}}/Z = 0.75$ for which EFGs in pure zinc agree quite well with experiments (Bodenstedt and Perscheid 1978). The range of EFG obtained by varying Z_{eff}/Z from 0.5 to 1 is typically $\sim 50\%$ around the reported values. The lattice spacings are taken from Pearson (1958) and the elastic constants from Simmons and Wang (1971).

Zinc has a large c/a ratio and the mean squared displacement is highly anisotropic (de Wames *et al* 1965) with $\langle x_{\perp}^2 \rangle / \langle x_{\parallel}^2 \rangle \approx 0.35$. A strong temperature dependence of EFG

Table 1. CSM calculations of EFG (in units of 10^{17} V/cm²) in FeZn. Z_{eff}/Z is taken to be 0.75 for probe as well as for host

Temperature (K)	EFG without probe nucleus vibration	EFG with probe nucleus vibration
4.2	3.02	2.98
77	3.02	2.94
295	3.01	2.68
400	2.98	2.51

in zinc is therefore expected. Indeed the EFG in pure system ZnZn shows strong temperature dependence (Christiansen *et al* 1976). However the measured field gradient 2.39×10^{17} V/cm² in FeZn shows practically no change with temperature (Dunlop *et al* 1978).

The results of our calculations based on charge shift model displayed in table 1, are in excellent agreement with the experimental observations if we neglect the effect of anisotropic vibrations of iron impurity in zinc. The calculated EFG is almost constant in the temperature range 4.2–400 K and is close to the experimental values.

We have also made calculations incorporating the probe nucleus vibration as described in Bodenstedt and Perscheid (1978). In the absence of a detailed formulation of lattice dynamics of impurity vibrations in non-cubic hosts, we have used the Einstein-Debye relation

$$\frac{\langle x^2 \rangle_{\text{impurity}}}{\langle x^2 \rangle_{\text{host}}} = \left\{ \frac{M_{\text{impurity}}}{M_{\text{host}}} \right\}^{1/2}$$

assuming equal force constants for Fe–Zn and Zn–Zn. The mean squared displacement of Fe in Zn at and above room temperature is taken to be equal to that of Zn in Zn (Dawber and Elliot 1963).

The agreement between CSM and experiments becomes poor on introduction of probe nucleus vibrations. As the model successfully describes the magnitude and temperature dependence of EFG in pure zinc and also the magnitude of EFG in FeZn at room temperature, it is reasonable to assume that the assumptions of CSM are also appropriate to describe the temperature dependence of EFG in FeZn.

One reason for the discrepancy between the experimental and the CSM values may lie in the inadequacy of the simple approach taken here to describe the impurity vibration in zinc host. In particular, it is assumed that the anisotropy parameter has the same value of 0.35 for iron in zinc and for pure zinc. In view of the better agreement with measured values obtained by assuming isotropic vibrations of Fe in zinc, and the sensitiveness of CSM towards anisotropic vibrations, one may infer that the anisotropy parameter of iron in zinc is likely to be considerably lower than that for pure zinc.

4. Conclusion

The metallurgically prepared FeZn alloy undergoes irreversible phase transition on heating. A new phase precipitates which gives a single line Mössbauer spectrum at

0.359(6) mm/sec with respect to rhodium. The measurements support the results of Dunlop *et al* (1978) that the EFG at iron in FeZn does not depend on temperature. This observed constancy of EFG is well described by the charge shift model if we ignore the probe vibrations.

Acknowledgements

The author is thankful to Professor G N Rao, Dept. of Physics, IIT Kanpur for his association during experimental part and to Sri S N Gupta and Sri G Varma for their help during numerical calculations.

References

- Bodenstedt E and Perscheid B 1978 *Hyperfine Interact.* **5** 291
Christiansen J, Heubes P, Keitel R, Klinger W, Loeffler W, Sandner W and Witthun W 1976 *Z. Phys.* **B24** 177
Dawber P G and Elliot R J 1963 *Proc. R. Soc. (London)* **A273** 222
de Wames R E, Wolfram T and Lehman G W 1965 *Phys. Rev.* **138** A717
Dunlop J B, Williams J M and Longworth G 1978 *J. Phys.* **F8** 2115
Kündig W, Ando K and Bömmel H 1965 *Phys. Rev.* **139** A889
Maio A, Hermans L, Rots M, Rao G N and Coussement R 1982 *Hyperfine Interact.* **11** 239
Pearson W B 1958 *A handbook of lattice spacings and structures of metals and alloys* (New York: Pergamon Press)
Simmons G and Wang H 1971 *Single crystal elastic constants and calculated aggregate properties*, 2nd ed. (Cambridge: MIT Press)
Verma H C and Rao G N 1981 *Phys. Lett.* **A82** 303