PHYSICAL REVIEW VOLUME 138, NUMBER 3A 3 MAY 1965

Mean-Square Nuclear Displacement of Fe^{57} in Zn from the Mössbauer Effect*

R. M. Housley†
University of Washington, Seattle, Washington

AND

R. H. Nussbaum‡
Portland State College, Portland, Oregon

(Received 14 December 1964)

Fe^{57} in Zn shows a quadrupole splitting of 0.53 ± 0.03 mm/sec and a chemical shift of -0.53 ± 0.02 mm/sec relative to an Fe metal absorber at room temperature. The measurements of the Mössbauer fraction f indicate a ratio of mean-square displacements $\langle x^2\rangle_{\parallel}/\langle x^2\rangle_{\perp}\geqslant 2$ at room temperature relative to the crystal c axis. This is in qualitative agreement with lattice-dynamical calculations.

INTRODUCTION

In a previous paper[1] we indicated how the mean-square displacement $\langle x^2\rangle$ of an emitting nucleus can be obtained from a Mössbauer f measurement. We also showed how in case the emitting nucleus is a dilute impurity one can find an effective ratio of host-impurity force constant to pure-host force constant from $\langle x^2\rangle$. It is only necessary that the $\langle x^2\rangle$ of the pure host be known from some other measurements. Here we make the presently unverified assumption that $\langle x^2\rangle$ of the host material can be accurately calculated if its phonon-dispersion curves have been measured by neutron-scattering techniques.[1] Hence in investigating the systematic behavior of effective host-impurity force-constant ratios it seems desirable to use hosts whose phonon dispersion curves have been measured. In a previous investigation Fe in Cu and Be were studied for that reason.[1] Zn is another desirable host for the same reason. Its phonon dispersion curves have been measured[2] and lattice dynamical calculations giving $\langle x^2\rangle$ as a function of temperature and orientation have been made.[3] The large predicted anisotropy in $\langle x^2\rangle$ further increases the interest in studying Zn.

EXPERIMENTAL

Precise absolute f measurements were made by the black-absorber technique which has been described previously.[4,1]

Preparation of a Zn single-crystal source with all the Co^{57} impurity atoms in solid solution is very difficult and our metallurgical preparations have only been partially successful. The solubility of Fe or Co in Zn is small with excess amounts tending to precipitate in the Zn-rich γ_2 phase.[5] In addition, Zn has a low melting point (420°C) and a high vapor pressure at temperatures near the melting point.

Polycrystalline Source

Before attempting to dope the single crystal with the Co^{57} impurity we made two attempts to dope pieces of chemical-grade zinc foil (containing 0.01% Fe). Activity was deposited on the foils by depositing Co^{57} by self-plating from a neutral $Co^{57}Cl_2$ solution. The surface was then washed vigorously in order to remove any chlorides from the surface.[1] The first foil was heated at 400°C in an H_2 atmosphere for about one day. It was obvious that a lot of the material had evaporated from the sample. A black spot was visible where the cobalt had been deposited. The Mössbauer pattern of this source was a broad asymmetrical line. Since is appeared that during the heat treatment the Zn was evaporating from the surface at least as fast as the Co from the surface was diffusing into the foil, the second source was completely wrapped in additional Zn foil and otherwise given the same treatment as the first. This source also had a visible mark where the activity had been deposited and gave a similar broad and asymmetrical Mössbauer pattern. Following this both sources were rolled up and sealed in small quartz ampoules in an H_2 atmosphere. In these ampoules they were heated to 900°C for one hour, then quenched in water. In both cases a black rod-shaped residue remained where the rolled foil had been. It contained most of the Co^{57}. The button of Zn which formed in the bottom of the ampoule contained only a few percent of the activity. These buttons were then rolled into foils and Mössbauer spectra were measured with a $K_4Fe(CN)_6$ absorber. Both sources showed identical spectra with well resolved quadrupole splitting. We interpreted these spectra to be due to Fe in solution in polycrystalline Zn.

One of these foils was subsequently heated at 400°C

---

* This work was partly supported by an AFSOR grant AF-AFOSR-594-64.

† Present address: Natuurkundig Laboratorium, University of Groningen, Groningen, The Netherlands.

‡ Supported by a National Science Foundation Grant to the University of Washington for Improvement of the Teaching of Science.

[1] R. M. Housley, J. G. Dash, and R. H. Nussbaum, Phys. Rev. **136**, A464 (1964).

[2] G. Borgonovi, G. Cagliotti, and J. J. Antel, Phys. Rev. **132**, 683 (1963).

[3] R. E. DeWames, T. Wolfram, and G. W. Lehman (to be published).

[4] R. M. Housley, N. E. Erickson, and J. G. Dash, Nucl. Instr. Methods **27**, 29 (1964).

[5] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

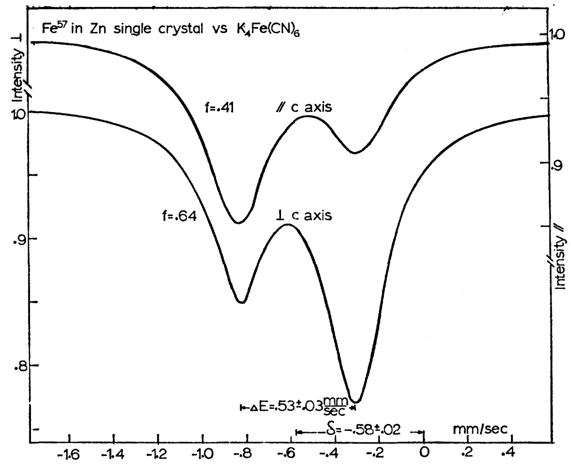

FIG. 1. Computer-fitted Mössbauer spectra of Fe^{57} in Zn single crystal versus a $K_4Fe(CN)_6$ absorber, both parallel and perpendicular to the crystal *c* axis. Note the shifted intensity scales for the parallel, and perpendicular orientations.

for three hours. The region between the quadrupole lines of the spectrum was found to be filled in by another line or lines. This we believe was owing to the precipitation of the γ_2 phase during annealing at 400°C.

Single Crystal Source

The Zn single crystal was a disk cut at 45 deg to the crystal *c* axis. Measurements could therefore be made both $||$ and $\perp$ to the *c* axis with the same source. It had a stated purity of 99.95%. The activity was self-plated on this sample as described for the polycrystalline material. The crystal was then wrapped in Zn foil and heated for three days at 400°C in an H_2 atmosphere. After this treatment the surface was dark and irregular. This surface was cleaned by etching with HCl. The spectrum of this source showed a resolved quadrupole pattern similar to that obtained from the polycrystalline sources prepared by melting. Typical spectra are shown in Fig. 1 both $||$ and $\perp$ to the crystal *c* axis.

RESULTS

Spectra and *f* measurements were obtained both $||$ to and $\perp$ to the *c* axis at room temperature. The quadrupole splitting of Fe in Zn is 0.53 ± 0.03 mm/sec and the chemical shift is -0.53 ± 0.02 mm/sec versus Fe metal absorber.[6]

The ratio of intensities in the quadrupole lines was found $3:5\perp$ to the *c* axis and $2:1$ in the $||$ direction. These ratios are in qualitative agreement with those expected for a ***positive*** electric-field gradient.[7] However, the intensity ratio $||$ to the *c* axis of a single crystal should be $3:1$ instead of $2:1$. The deviation is an indication that the source was not ideal. Several effects could result in the observed reduction of the intensity ratio: (1) misalignment of the material grown during the heat treatment, or (2) a small amount of Co^{57} precipitated in the γ_2 phase, or (3) Co^{57} which replated on the source surface during the etching treatment, and therefore was not in solid solution. Further etching of the surface caused a deterioration of the Mössbauer spectrum. This tends to verify that replating during etching was an important contributing factor to the observed deviation from the ideal Mössbauer pattern.

The *f* values obtained with this source at room temperature were $f_\perp=0.64$, $f_{||}=0.41$. Several attempts to improve the perfection of this source, and to get better *f* values failed. This precluded a reliable interpretation of our *f* measurements with this source at liquid-He temperatures.

DISCUSSION

The sign of the electric-field gradient is opposite to that for Fe in Be.[1] This corresponds to an opposite distortion from the ideal hcp structure. The sign in both materials is also opposite to the sign of the lattice contribution as calculated from a simple model.[8]

Assuming that the imperfection of the source would reduce rather than enhance the anisotropy in *f* we can conclude that $\langle x^2\rangle_{||}/\langle x^2\rangle_\perp \geqslant 2$. A ratio of 2.8 in the same sense was predicted for pure Zn by lattice dynamical calculations.[3]

ACKNOWLEDGMENTS

We wish to thank Dr. J. G. Dash for his stimulating interest and support, and N. E. Erickson for very helpful discussions. We are also grateful to R. E. DeWames and U. Gonser for informing us about the large predicted anisotropy in Zn from lattice dynamical calculations. One of the authors (R.H.N.) wants to thank the Physics Department of the University of Washington, and the Low Temperature Research Group in particular, for their hospitality.

---

[6] We are grateful to W. Kündig who informed us of his measurement of the quadrupole splitting of Fe^{57} in polycrystalline Zn in agreement with our results. W. Kündig, K. Ando, and H. Bömmel, Bull. Am. Phys. Soc. **10**, 64 (1965).

[7] See, e.g., G. K. Wertheim, *Mössbauer Effect* (Academic Press Inc., New York, 1964), Chap. VI.

[8] F. W. DeWette, Phys. Rev. **123**, 103 (1961).