

Mean-Square Displacement of Dilute Iron Impurity Atoms in High-Purity Beryllium and Copper

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Absolute values of the Mössbauer fraction f of zero-phonon gamma rays from dilute Co^{57} in Be and Cu were obtained for several temperatures between liquid helium and room temperature using the technique of the "black absorber." For Be at 297°K, $f=0.81$; for Cu at 297°K, $f=0.71$. Systematic errors are estimated to be less than 2%. The Mössbauer spectrum of Be shows a quadrupole splitting $\Delta E=0.56\pm 0.03$ mm/sec and a chemical shift $\delta=-0.11\pm 0.03$ mm/sec with respect to an Fe absorber.

INTRODUCTION

USING the technique of the "black absorber,"¹ a Mössbauer experiment can yield a precise value of the mean-square displacement $\langle x^2 \rangle$ of the radioactive impurity atoms in a host lattice. The fraction f of photons emitted without energy loss to the lattice is given by the expression² $-\ln f = \langle x^2 \rangle / \lambda^2$ where $2\pi\lambda$ is the wavelength of the emitted gamma ray. This relation is independent of the detailed structure of the phonon spectrum of the host lattice, and it holds to a good approximation even in the case of anharmonic atomic forces.³ The Mössbauer f factor is the equivalent of the well-known Debye-Waller factor which determines the temperature dependence of x-ray-diffraction line intensities.

LATTICE DYNAMICS

Of more fundamental interest than the mean-square displacements are the forces themselves which bind the impurity atoms to their sites in the lattice. It may be hoped that an experimental determination of these forces in several materials will help to increase our understanding of the interatomic forces in solids. Less ambitiously, it is possible that significant correlations can be found between the binding forces and other characteristics of the impurities or of other properties of the system which depend on the presence of the impurities.

The best information about the host-impurity force constants can only come from detailed lattice dynamical calculations making use of known atomic force constants for the pure host material. The mean-square displacements of the host atoms as a function of temperature can readily be calculated from these force

constants.⁴⁻⁶ Several model calculations have been done relating the mean-square displacements of isotopic impurities in a lattice to the mean-square displacement of the host atoms.⁷⁻⁹ These models assume the same forces between impurity and host as between host atoms. The results of these calculations are independent of the details of the frequency spectrum of the host in both the high- and low-temperature limits.

$$\text{For } T \gg \theta_D \quad \langle x^2 \rangle_{\text{imp}} = \langle x^2 \rangle_{\text{host}}, \quad (1)$$

$$\text{For } T \rightarrow 0 \quad \langle x^2 \rangle_{\text{imp}} / \langle x^2 \rangle_{\text{host}} = (m_{\text{host}} / m_{\text{imp}})^{1/2}. \quad (2)$$

Experimental deviations from the relationships (1) and (2) would indicate that the impurity-host force constants are not the same as the force constants in the pure-host material as was assumed in their derivation and hence an estimate of the force constant *changes* can be obtained.

Recent work by Lehman and DeWames¹⁰ should allow much better determinations of host-impurity force constants than those obtainable from investigations at the above temperature limits. They have devised a numerical method for calculating the mean-square displacement of an impurity in a real lattice as a function of temperature for various assumed host-impurity force constants. So far, results have only been published for Fe in Al and for Sn in Ge.¹⁰

⁴ P. A. Flinn, G. M. McManus, and J. A. Rayne, *Phys. Rev.* **123**, 809 (1961).

⁵ R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.* **131**, 528 (1963).

⁶ P. A. Flinn and G. M. McManus, *Phys. Rev.* **132**, 2458 (1963).

⁷ H. J. Lipkin, *Ann. Phys. (N. Y.)* **23**, 28 (1963).

⁸ P. G. Dawber, and R. J. Elliott, *Proc. Roy. Soc. (London)* **A273**, 222 (1963).

⁹ I. P. Dzyub and A. F. Lubchenko, *Dokl. Akad. Nauk. SSSR* **147**, 584 (1962) [English transl.: *Soviet Phys.—Doklady* **7**, 1027 (1963)].

¹⁰ G. W. Lehman and R. E. DeWames, *Phys. Rev.* **131**, 1008 (1963).

¹ R. M. Housley, N. E. Erickson, and J. G. Dash, *Nucl. Instr. Methods* **27**, 29 (1964).

² H. J. Lipkin, *Ann. Phys. (N. Y.)* **9**, 332 (1960).

³ A. A. Maradudin and P. A. Flinn, *Phys. Rev.* **129**, 2529 (1963).

At present, measurement of phonon dispersion curves by the inelastic scattering of slow neutrons seems to be the only way of getting sufficient data for an accurate determination of the pure-host force constants. Such dispersion curves have been obtained for relatively few materials.

EXPERIMENTS

The apparatus and experimental techniques as well as the small corrections applied to the raw data were discussed in Ref. 1. As in the earlier paper, the uncertainties reflect both the statistical errors and the uncertainties in the small corrections due to inelastically scattered 14-keV radiation and the slight uncertainty in absorber blackness.

One additional correction not mentioned previously may be a significant factor. Depending on the amount and distribution of Co^{57} in a source it is quite possible that sufficient Fe^{57} will be present, at least after the activity has decayed for a while, to produce significant self-absorption. This possibility was minimized in our work by using weak sources. Nevertheless, we made a check for self-absorption by measuring the change in count rate without an absorber when a magnetic field was applied to our sources. This reduces self-absorption by splitting the resonance lines. The only significant self-absorption was found in the case of Be perpendicular to the c axis, where it amounted to a little more than 4% of the resonant fraction. This led to a 1% correction in the measured f value.

Beryllium

Beryllium is known to have a low solubility for Fe and Co.¹¹ In an attempt to insure that the Co was dissolved, we prepared several sources of Co^{57} in Be by a variety of methods. The activity was deposited either by evaporation of CoCl_2 solution and subsequent heating in H_2 , or by electroplating. Thermal diffusion was carried out at temperatures from 1000 to 1100°C, for times varying from 1 to 10 h, and in vacuum, H_2 , or He atmosphere. After diffusion, the samples were cooled to room temperature in times from 10 sec to several hours. These sources exhibited substantially the same resonance emission spectra to within our experimental resolution. The particular source used for f measurements was prepared by electroplating about 1 mCi "premium grade" Co^{57} ¹² on a high-purity single-crystal flake of Be.¹³ The activity was diffused into the crystal by heating for 7 h at 1000°C in an atmosphere of purified H_2 . Autoradiographs of this source indicated that the activity was fairly uniformly distributed over the surface. The average concentration of Co and

¹¹ M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

¹² Supplied by Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania.

¹³ Supplied by D. D. Blue of the U. S. Bureau of Mines, Metallurgy Research Center, Boulder City, Nevada.

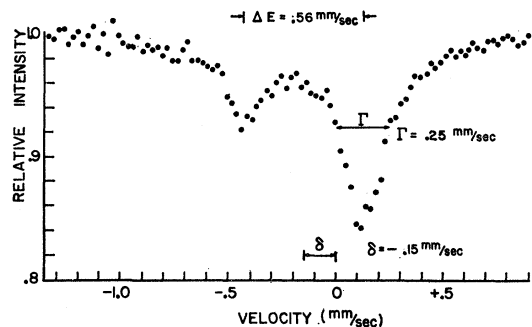


FIG 1. Velocity Spectrum of Co^{57} in a single-crystal Be sample versus a FeF_2 absorber (one of the two components of the absorption spectrum) at room temperature. The spectrum was taken parallel to the c axis. The theoretical ratio of the intensities of the components of a two-line quadrupole spectrum parallel to the symmetry axis is 1:3. The observed dips have a smaller intensity ratio, probably due to a slight misalignment of the crystal.

Fe was accordingly estimated to be ≤ 0.01 at. %, which is well within the solubility range.¹¹

The velocity spectrum taken versus a single-line component of the absorption spectrum of FeF_2 is shown in Fig. 1. After correcting for broadening due to absorber thickness, the lines appear to have natural width. We find a quadrupole splitting of $\Delta E = 0.56 \pm 0.03$ mm/sec and a chemical shift of $\delta = -0.11 \pm 0.03$ mm/sec relative to Fe metal, in agreement with the results of Kistner and Mozer.¹⁴ These authors found that Fe precipitated from solution in Be shows a distinctly different resonance spectrum. Our sources have the spectrum which they concluded to be characteristic of Fe dissolved in Be.

A series of f measurements were made on this sample between room temperature and liquid-helium temperature. The f values obtained are given in Table I. Phonon dispersion curves have been obtained for Be.¹⁵ Lattice dynamical calculations of the mean-square displacements of the Be atoms and of substitutional

TABLE I. f Factors. Experimental f values obtained for Fe^{57} in Be parallel to the c axis and for Fe^{57} in Cu at various temperatures. (Ref. 21). The Be values are compared with the results of preliminary calculations (Ref. 16) made, assuming that the force constants binding the Fe are the same as the pure Be force constants. All experimental values have uncertainties within $\pm 2\%$ due primarily to possible systematic errors (see text).

Temp. °K	Be to c axis exp	calc	Cu exp
<40	0.920	0.90	
78±1	0.915	0.89	0.880
103±3	0.905		
143±3	0.891		
183±3	0.870		
223±3	0.853		
297±1	0.812	0.75	0.710

¹⁴ O. C. Kistner and B. Mozer, *Bull. Am. Phys. Soc.* 7, 505 (1962).

¹⁵ R. E. Schmunk, R. M. Brugger, P. D. Randolph, and K. A. Strong, *Phys. Rev.* 128, 562 (1962).

Fe impurity atoms are underway.¹⁶ Preliminary results of these calculations, assuming no force constant change, are also shown in Table I. At room temperature, the measured f was found to be about 1% smaller parallel to than perpendicular to the c axis with an experimental uncertainty of about 1%. This result, though barely statistically significant, may indicate that the anisotropy is in the opposite direction to the anisotropy expected in the vibrations of the Be atoms. Simple calculations based on the bulk elastic constants¹⁷ predict an anisotropy of 0.5% and preliminary calculations by DeWames¹⁶ predict an anisotropy of 2%, both in the opposite direction to the observations.

Copper

Many groups doing Mössbauer-effect measurements on Fe⁵⁷ use dilute Co⁵⁷ dissolved in Cu as radiation sources. We have carried out a study to determine whether such sources can be made to yield reproducible f values. In that case, these sources could be used as standards for f measurements by the relative area technique,^{1,18} and a black absorber would not be necessary to obtain accurate absolute f values.

We studied three Cu sources. They were all made by evaporating about 1 mCi of Co⁵⁷Cl₂ on the surface, and then reducing and diffusing in a hydrogen atmosphere. We found that all the doping solutions left an appreciable solid residue on the surface. Sufficient Co⁵⁷ remains in this residue to cause an apparent reduction of f of about 10% if it is not removed. We found that scrubbing with a commercial cleanser containing diatomaceous earth and washing with HCl is a satisfactory cleaning procedure.

The first specimen used was commercial purity Cu. It was doped with regular grade Co⁵⁷Cl₂ solution.¹² No attempt was made to spread the activity uniformly on the surface. It was found necessary to diffuse this specimen a total of 2 h at 900°C before further diffusion left the f value of source No. 1 unchanged.

Two more specimens were prepared from Cu of 99.999% purity. The second specimen was doped with premium grade Co⁵⁷Cl₂ solution,¹² and the third was doped with regular grade Co⁵⁷Cl₂ solution which we had purified in an ion exchange column. In doping these specimens we tried, with only partial success, to spread the activity more uniformly over the surface. After heating for only 15 min at 900°C, both of these sources had reached their final and maximum f values at room temperature, which were both the same

(within 1%) as that of source No. 1. The resonance linewidth as observed with a 6.4 mg/cm² natural iron foil was 0.20 mm/sec for these sources.

On two occasions we cold rolled source No. 1, resulting in about a 50% increase in area without producing any measurable change in f . After one such treatment, we heated the specimen at 350°C for 24 h. If there were any strong tendencies of Co atoms to diffuse to defects, this treatment might have produced a measurable change in f . No change was observed.

Lattice dynamical calculations using sufficiently accurate force constants are not yet available for comparison. However, phonon dispersion curves for Cu have recently been measured by neutron scattering.¹⁹ Comparison of these results with earlier x-ray diffraction data seem to indicate that the x-ray results disagree significantly.²⁰ We hope that mean-square displacement values of Cu will soon be calculated from the neutron data.

Copper as f Standard

One conclusion of the above experiments is that it is relatively easy to make a Cu source which has the true f value of dilute Fe impurities. Hence, Cu is suitable for use as a standard when f measurements are made by the relative area method. We find the f of Cu at room temperature to be 0.710. At liquid nitrogen temperature it is 0.880 (see Table I).²¹

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¹⁹ D. Cribier, B. Jacrot, and D. Saint-James, *J. Phys. Radium* **21**, 67 (1960).

²⁰ P. K. Sharma and S. K. Joshi, *J. Chem. Phys.* **40**, 662 (1964).

²¹ Preliminary results of these measurements were reported at the Third International Conference on the Mössbauer Effect, Ithaca, New York. The proceedings of the conference were published [R. M. Housley, J. G. Dash, and R. H. Nussbaum, *Rev. Mod. Phys.* **36**, 439 (1964)].

¹⁶ R. E. DeWames (private communication).

¹⁷ C. Zener, *Phys. Rev.* **49**, 122 (1936).

¹⁸ G. Lang, *Nucl. Instr. Methods* **24**, 425 (1963).