STRUCTURAL IMPLICATION OF ASYMMETRIC MÖSSBAUER SPECTRA OF SOME DECAGONAL QUASICRYSTALS

Z.M. STADNIK

Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

A.-P. TSAI and A. INOUE

Institute for Materials Research, Tohoku University, Sendai 980, Japan

ABSTRACT

Room-temperature ^{57}Fe Mössbauer spectra of ^{57}Fe-doped decagonal alloys $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$ give unambiguous evidence for the presence of two distinct distributions of electric quadrupole splittings. The possible structural implications of this experimental finding are discussed.

1. Introduction

Diffraction methods, including the extended x-ray absorption fine structure technique, upon which the bulk of our knowledge on the structure of quasicrystals (QCs) is based, yield only radial structural information. A complete structural picture requires additional angular structural information which can be obtained from studies of an electric quadrupole interaction between a nuclear electric quadrupole moment and an electric field gradient at the nucleus. Such studies can be carried out using the techniques of nuclear magnetic resonance (NMR) or Mössbauer spectroscopy (MS).

In spite of its great potential, MS has had little impact on the structural studies of QCs. One of the reasons for this is a qualitative similarity of Mössbauer spectra of different nonmagnetic QCs, which are in a form of a structureless and broad quadrupole doublet, and methodological problems in their proper analysis (for a recent review, see Ref. 1).

In this paper we report results of ^{57}Fe MS studies of ^{57}Fe-doped decagonal alloys $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$. Asymmetric Mössbauer spectra of these alloys have significant structure which reflects the local atomic structure around the transition-metal atoms. A proper analysis of these spectra provides two distinct distributions of the electric quadrupole interactions which are discussed in terms of possible structural models. The presence of a clear structure in the Mössbauer spectra of ^{57}Fe-doped $Al_{65}Co_{15}Cu_{20}$ was reported for the first time by Eibschütz et al.[2]

2. Experimental

Ingots of nominal composition $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ and $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$ were prepared by melting high-purity source metals in an argon atmosphere using an arc furnace. The iron metal used was enriched to 95.9% in the ^{57}Fe isotope. The ingots were annealed in vacuum at 1073 K for 48 h. The x-ray diffraction study showed that the samples are single phase and exhibit resolution-limited Bragg-peak widths.[3]

^{57}Fe MS measurements were performed at room temperature using a standard Mössbauer spectrometer operating in a triangular mode. The spectrometer was calibrated with a 6.35 μm Fe foil and the spectra were folded. The surface densities of the Mössbauer absorbers corresponding to $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ and $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$ were respectively $30.4 \cdot 10^{-3}$ and $36.5 \cdot 10^{-3}$ mg $^{57}Fe/cm^2$; the absorbers can therefore be regarded as being thin.

3. Results and Discussion

As opposed to Mössbauer spectra of all single-phase QCs studied so far, the spectra of $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ and $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$ (Fig. 1) exhibit a clear
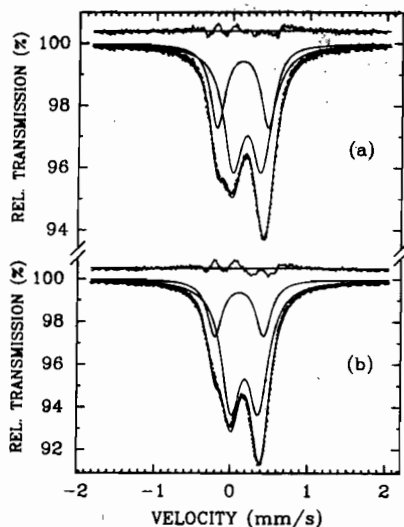
Fig. 1. ^{57}Fe Mössbauer spectra of (a) $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ and (b) $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$ fitted with two symmetric Lorentzian doublets, as explained in the text.
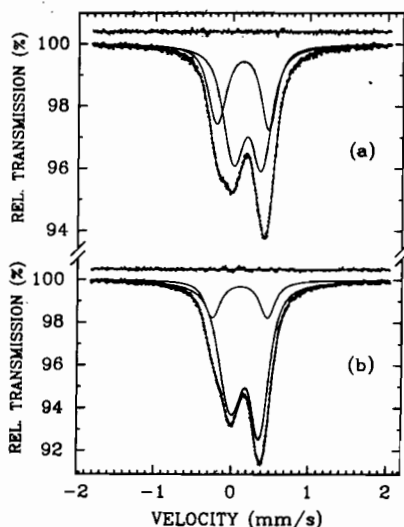
Fig. 2. ^{57}Fe Mössbauer spectra of (a) $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ and (b) $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$ fitted with two independent distributions of quadrupole splittings, as explained in the text.

structural asymmetry which, to a first approximation, can be accounted for by fitting them with two symmetric Lorentzian doublets.[2] As can be seen from the difference between the measured and fitted spectra (Fig. 1), such a fit is clearly unsatisfactory. It is also methodologically incorrect[1,3] as it results in unphysically broad widths for the component Lorentzian doublets. These broad widths reflect the presence of a multiplicity of non-equivalent transition-metal (TM) sites. This means that any meaningful analysis of Mössbauer spectra of QCs must be based on fits which assume a distribution of the hyperfine interaction parameters.

An excellent fit is obtained (Fig. 2) assuming two independent Gaussian distributions of quadrupole splittings, $P(\Delta)$, and resulting[1,3] Gaussian distributions of isomer shifts, $P(\delta)$. The linewidth of the elemental doublets is close to the natural linewidth.[3] For $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ the mean Δ and δ (with respect to α-Fe) values of the two $P(\Delta)$ and $P(\delta)$ distributions are respectively (all in mm/s) 0.369(1), 0.679(2), and 0.183(4), 0.132(2); the corresponding values of the full width at half maximum (FWHM) are (all in mm/s) 0.359(5), 0.220(5), and 0.011(1), 0.020(1). For $Al_{70}Co_{15}Ni_{14.9}Fe_{0.1}$, the mean Δ and δ values are respectively 0.380(1), 0.720(4) and 0.180(2), 0.107(3); the corresponding values of FWHM are 0.382(3), 0.167(10) and 0.044(1), 0.004(1). A detail analysis of the fitted parameters is given elsewhere.[3] As an example, the distributions corresponding to the fit of the $Al_{65}Co_{15}Cu_{19.9}Fe_{0.1}$ spectrum in Fig. 2(a) are shown in Fig. 3.
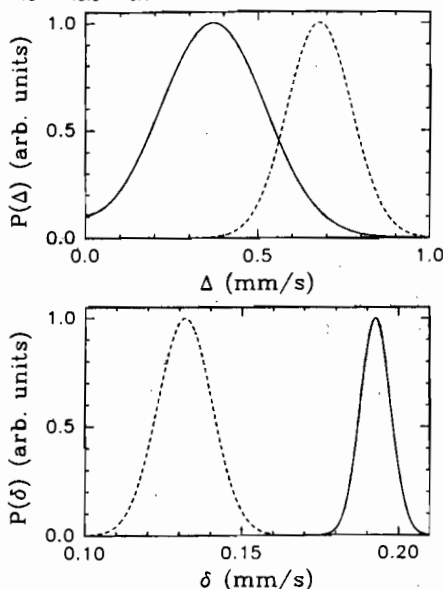

Fig. 3. Two distributions of $P(\Delta)$ and of $P(\delta)$ corresponding to the fit in Fig. 2(a).

The thermodynamically stable QCs, such as those studied here, are sometimes called "perfect" based on the fact that their diffraction lines are limited only by the resolution of a spectrometer, which implies a high degree of structural perfection comparable to that found in the best periodic alloys. The term perfect is however misleading because the existence of the distributions $P(\Delta)$ and $P(\delta)$ observed here, and also found[1] in other stable QCs of high structural quality, clearly indicates the presence of some sort of disorder. There are at least two types of disorder which must be present in the stable QCs of high structural quality. All Al-based stable QCs are ternary alloys. The presence of two TM atoms may induce some degree of chemical disorder. The second type of disorder, which can be viewed as a sort of topological disorder, stems from the concept of quasiperiodicity which implies that no two crystallographic positions of a given atom are exactly the same;[4] obviously, local probes are better suited to detect such a type of topological disorder. Although these two types of disorder are not seen easily in the diffraction and electron microscopy experiments, they are clearly detected, but not separated, in the experiments using such local probes as MS or NMR. Also other experiments performed on stable, single-grained QCs indicate the presence of some sort of disorder.[5] It seems therefore that disorder must be taken into account in constructing structural models of QCs. It may also have a profound influence on their electronic properties.[6]

The distributions $P(\Delta)$ and $P(\delta)$ derived above could be used, in principle, to discriminate between different structural models proposed for the decagonal $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$ alloys (for a recent review of these models, see Refs. 7 and 8). This would require calculating for a given model the electric quadrupole interaction and compare it with experiment. Such calculations are a complex and a challenging endeavour even for simple crystalline metallic systems. The first such calculations[9] done for a Burkov model[10] of the decagonal Al-Co-Cu alloy predict a Mössbauer spectrum which is at variance with the spectrum observed experimentally [Fig. 2(a)]. This means that either the Burkov model is inappropriate or that the calculations themselves need some refinement. In this situation we have to discuss qualitatively the implication of our Mössbauer results in relation to structural models of decagonal Al-Co-Cu(Ni).

The experimental observation of two distinct distributions of $P(\Delta)$ and $P(\delta)$ implies the existence of two basic building blocks in the structure of the Al-Co-Cu(Ni) decagonal alloys. This observation would thus favour structural models which are based on such two blocks. Recently a new structural model of decagonal Al-Co-Cu has been proposed.[8] It is based on the experimental observations derived from electron and x-ray diffraction, high resolution electron microscopy, and scanning tunnelling microscopy studies which, in contrast to other models, restrict the interatomic distances in this model to realistic values. This model assumes that there are two primary atom arrangements (clusters) formed from an icosahedron by removing the atoms on two opposing vertices to form pentagonal polyhedra.[8] The larger cluster (pentagonal polyhedron) consists

of 10 Al atoms surrounding a Co or Cu atom at the centre (the model does not differentiate between the Co and Cu atoms whose atomic radii differ only by about 2%). In the smaller cluster, five (Co,Cu) atoms replace the Al atoms in one pentagon, and an Al atom is located in the interior. These clusters are then properly connected to form aggregates, which in turn can be arranged to form a crystalline or quasicrystalline structure.[8] Since MS is a local probe, it can detect the existence of the two primary clusters provided that the hyperfine parameters associated with them are different. The geometry of these clusters implies that they should lead to two different values of the quadrupole splitting, which is exactly what is observed in the Mössbauer spectra (Figs. 2 and 3). As mentioned before, calculations of the electric quadrupole interaction for the two-cluster model[8] are required to convincingly determine its compatibility with the Mössbauer results.

Acknowledgements

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