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A new application of Mössbauer effect thermal scans: determination of the magnetic hyperfine field temperature dependence

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Abstract

Mössbauer thermal scans proved to be suitable to determining the magnetic hyperfine field temperature dependence at the Fe site of the antiferromagnet $FeSn_2$, if the Doppler energy is fixed at a value such that some of the nuclear transition energies cross that of the incident gamma ray when temperature is varied. © 2002 Elsevier Science B.V. All rights reserved.

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Mössbauer effect (ME) spectroscopy is a technique based on nuclear resonance emission–absorption recoilless processes. Among other applications, it is widely employed to study local properties of solids [1]. These studies can be performed because the magnetic dipolar as well as the electric monopolar and quadrupolar nucleus–electron interactions split and shift the nuclear levels and therefore allow the experimental determination of quantities such as the magnetic hyperfine field B, isomer shift δ and electric field gradient tensor V_{ij}. In a conventional experiment, Mössbauer spectra are taken using a standard gamma ray source and a sample absorber, varying the energy of the gamma rays by means of the Doppler effect, usually moving the source with constant acceleration. The spectra are recorded keeping external parameters as temperature, pressure, etc., fixed.

The magnetic hyperfine field and its dependence with temperature, $B(T)$, are important local properties related to other local and macroscopic magnetic properties, such as atomic moments and magnetization. In addition, $B(T)$ can be measured by ME in the absence of an external field which allows the study of intrinsic coupling and ordering mechanisms. A measurement of $B(T)$ is performed by taking a sufficient number of ME spectra at different temperatures (see Fig. 1). This methodology produces a wealth of information but requires rather long acquisition times. In several

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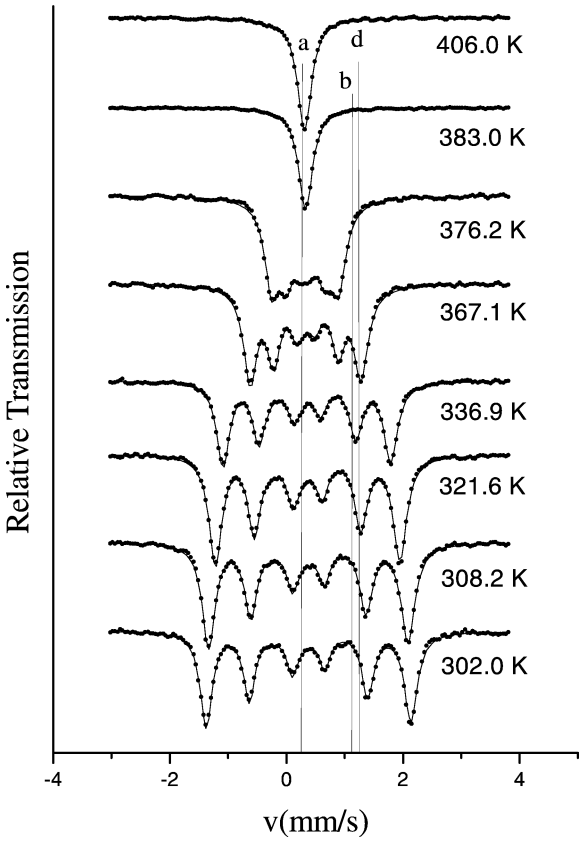

Fig. 1. ^{57}Fe Mössbauer spectra of $FeSn_2$ measured at different temperatures. Vertical lines a, b and d indicate three of the fixed velocities at which the thermal scan of Figs. 2 and 3 were performed.

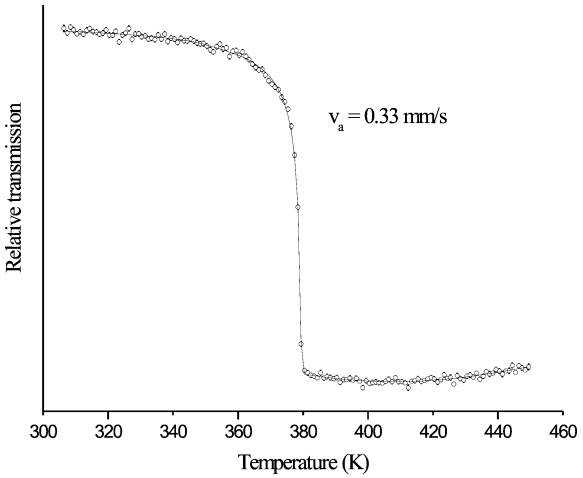

Fig. 2. Thermal scan carried out at a velocity close to that were maximum change in absorption occurs at T_C (see vertical line a in Fig. 1). The full line represents the fitted theoretical function, expression (2).

works a technique known as Mössbauer thermal scan (MTS) has been used to obtain fast and precise information on magnetic ordering temperatures [2–4]. It is a method particularly useful when a magnetically splitted spectrum collapses into a non-splitted one as temperature overcomes the critical value T_C. The energy is kept fixed near the value where maximum absorption occurs in the paramagnetic state (Fig. 1, vertical line a). Therefore, absorption undergoes a sudden change when T_C is crossed (see Fig. 2). To our knowledge, no attempt to develop a theoretical description of the MTS, useful for data analysis, has been made.

In this Letter we present a new application of the MTS, which allows the continuous determination of $B(T)$, within a wide temperature range, in a much faster manner than the traditional spectroscopic method. This application is experimentally similar to the previously mentioned MTS measurements though requires a simple but more careful treatment of the data. The only experimental difference resides in setting the fixed energy at values where the absorption evolution gives enough information to allow the determination of the temperature dependence of B with sufficient accuracy. This is achieved by choosing appropriately the source velocity v at a value which will be discussed below. The Doppler energy then becomes $E_v = vE_0/c$, where E_0 is the source transition energy and c the speed of light. To our purpose we have selected the antiferromagnet $FeSn_2$ with a critical Néel temperature T_C of about 380 K. This compound constitutes a good choice because its rather low T_C and the fact that Fe atoms occupy a unique crystallographic site with cubic antiprism symmetry, facilitate both the experiment and the analysis of the results. If at a temperature below T_C the gamma ray energy $E = E_0 + E_v$ is set between lines four and five of the ^{57}Fe ME spectrum (see Fig. 1, vertical lines b and d), when T is swept upwards the absorption undergoes the oscillations shown in Fig. 3.

The results of Fig. 3 can be qualitatively understood by noting that the absorption maxima of lines five and six depend on temperature as

$$E_i = E_0 + \delta_0 + \delta_{\mathrm{SOD}}(T) + \gamma_i B(T), \quad i = 5, 6, \qquad (1)$$

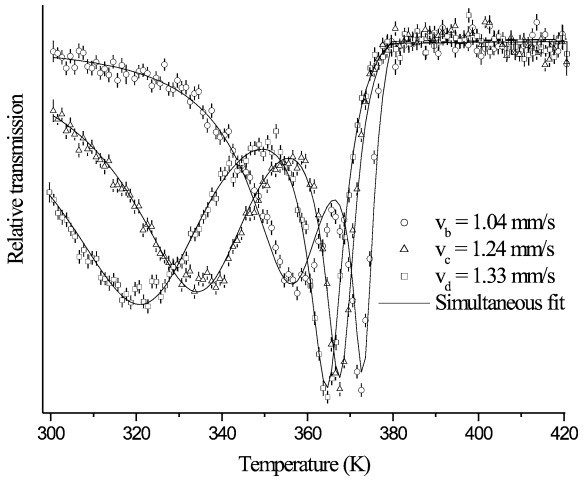

Fig. 3. Thermal scans performed at velocities v_b, v_c and v_d chosen in order to optimize the information on the temperature dependence of the magnetic hyperfine field (see vertical lines b and d in Fig. 1). The full lines represent the theoretical function, expression (2), simultaneously fitted to the three scans.

where δ_{SOD} is the energy second-order Doppler shift [5] due to the nuclei thermal vibrations, and γ_i are well-known constants. When T increases the position of these lines change and the scan absorption maxima occur at $E_i \approx E_0 + E_v$ (see Figs. 1–3). The asymmetries and different widths of the temperature images of lines five and six appearing in Fig. 3, mostly reflect the rate of change of B with the temperature.

The aim of the present Letter is to show the potential of this new application and discuss the analysis method, taking into account the different physical processes which contribute to the actual form of the thermal scans. The hyperfine field value at each temperature could be determined from each thermal scan data point or be retrieved with a fitting procedure, using a physical model for the evolution of $B(T)$. The method to be proposed here uses the second option. It will be also applied to make a quantitative description of conventional thermal scans, i.e., of the type designed to measure T_C (Fig. 2).

The device and software used to control velocity and temperature in the experiments were developed at the Electronics Laboratory of our department. Details about them will be published elsewhere [6]. The measurements were performed on a vertically arranged experimental setup mounted on robust steel rails which ensure the alignment of all components and minimize undesirable mechanical vibrations. Experimental linewidths, recorded with a ^{57}Co in Rh source of about 1 mCi and a 12 mm thick iron foil, were of the order of 0.24 mm/s. The temperature increase rate was set at 0.125 K/min which gave a total acquisition time of 12 h for each of the thermal scans of Fig. 3. All $FeSn_2$ absorbers used in this work were prepared with an ideal thickness of about 18 mg/cm^2 [7]. In the analysis of the scans other temperature-dependent phenomena must be considered besides $\delta_{\mathrm{SOD}}(T)$ and $B(T)$. These are absorption related ones: the absorber Mössbauer–Lamb factor evolution $f_a(T)$ and the change that absorption experiences due to saturation effects. This change is especially important for the interpretation of scans of the type shown in Fig. 2, because when a magnetically splitted spectrum (a sextet) collapses at T_C into a non-splitted one, absorption probabilities overlap at a unique energy which is close to the working energy. The increase that the saturation effect experiences when T_C is crossed is clearly demonstrated by the sudden decrease of the spectral area (see Fig. 4). To take into account these absorption phenomena, the exact expression for the intensity $I(E_v)$ of the gamma radiation arriving at the detector with Doppler energy E_v, after crossing the absorber [8],

$$I(E_v) = I_0 e^{-\mu x}\left(1 - f_s + \frac{f_s}{\pi}\int_{-\infty}^{\infty}\frac{1}{1+\epsilon^2} \times \exp\left(-z(T)\sum_{i=1}^{6}\frac{a_i}{1+(\epsilon-\epsilon_{vi})^2}\right)d\epsilon\right) + I_1,$$

$$\epsilon = \frac{E - E_0}{\Gamma_s/2}, \qquad \epsilon_{vi} = \frac{E_i - E_v}{\Gamma_a/2}, \tag{2}$$

must be used instead of the usual approximation consisting on a sum of Lorentzian lines. In expression (2) I_0 is the gamma ray source intensity emitted within the solid angle subtended by the detector, μ the mass absorption coefficient, x the absorber thickness, Γ_s and Γ_a are the effective half maximum energy full widths of the emission (source) and absorption (sample) lines, a_i the relative probabilities of the absorber transitions between the Zeeman splitted nuclear levels, and E_i are the absorption energies, given by (1) for $i = 1$–6, respectively. $z(T)$ is equal to the product $\sigma_0 n x f_a(T)$, σ_0 being the nuclear absorption cross section and n the number of ^{57}Fe atoms per volume unit. f_s and f_a are

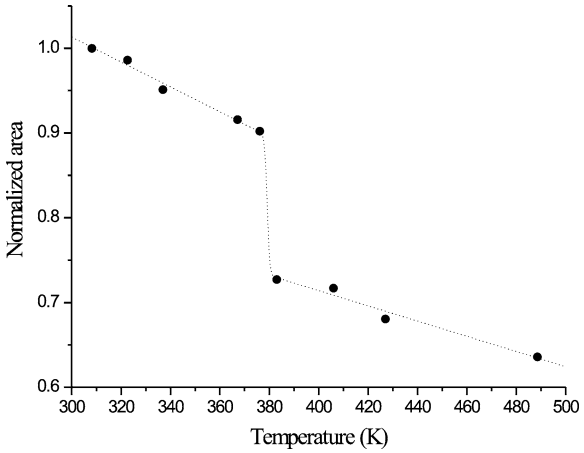

Fig. 4. Normalized area of spectra shown in Fig. 1 as a function of temperature. Notice the sudden change at $T = T_C$.

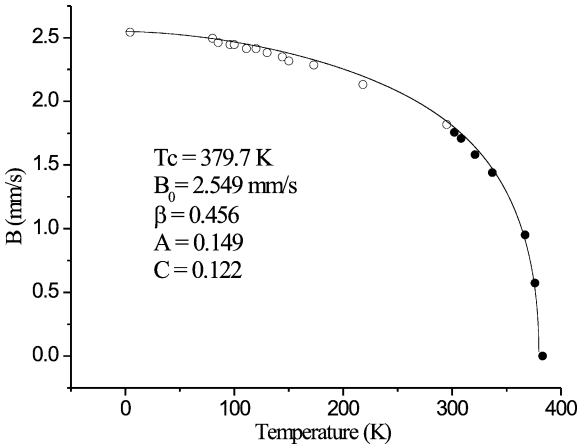

Fig. 5. Temperature dependence of the magnetic hyperfine field. Closed dots correspond to values obtained from the ME spectra show in Fig. 1 and open ones to those reported in Ref. [10]. The full line is a plot of expression (4) for values of the field parameters obtained from the fits of Figs. 2 and 3. These values are shown in the inset.

the Mössbauer–Lamb factors of source and absorber, respectively. The constant I_1 has been included to take into account all the radiation arriving at the detector (i.e., inelastically scattered at the collimator, originated in other nearby sources, etc.).

Within the scanned temperature range both the absorber Mössbauer–Lamb factor $f_a(T)$ and the second-order Doppler shift $\delta_{\mathrm{SOD}}(T)$ can be approximated by linear functions. Therefore the quantities $\delta(T) = \delta_0 + \delta_{\mathrm{SOD}}(T)$ and $z(T)$ can be written as

$$\begin{aligned} \delta(T) &= \delta(0) + \alpha_\delta T, \\ f_a(T) &= f_a(0) + \alpha_f T, \\ z(T) &= \sigma_0 n x f_a(T) = z_0 + \alpha_z T. \end{aligned} \tag{3}$$

From the spectra of Fig. 1 we have determined both $\delta(0)$ and the temperature coefficient $\alpha_\delta \cong (3.36 \pm 0.05) \times 10^{-11}$ eV/K, which corresponds to $(7.0 \pm 0.1) \times 10^{-4}$ mm/s K, in agreement with the expected high temperature limit of the last quantity [5]. For the sake of simplicity $B(T)$ was modelled with an empirical expression which has been proved to reproduce successfully the experimental magnetization of iron whiskers in the whole temperature range up to its ordering temperature [9],

$$B(T) = B_0 \frac{\left(1 - \frac{T}{T_C}\right)^\beta}{1 - \beta\left(\frac{T}{T_C}\right) + A\left(\frac{T}{T_C}\right)^{3/2} - C\left(\frac{T}{T_C}\right)^{7/2}}, \tag{4}$$

where B_0, β, A and C are model parameters.

The thermal scans shown in Figs. 2 and 3 were carried out at nominal Doppler velocities v_a, v_b, v_c and v_d of about 0.35, 1.0, 1.2 and 1.3 mm/s, respectively (see vertical lines in Fig. 1). These values were chosen in order to get good sensitivity to the hyperfine field evolution in the whole temperature range between RT and T_C, performing just a few scans. Non-linear fits based on the Levemberg–Marquardt method were carried out with a function built on expressions (1)–(4). The integral appearing in (2) was calculated numerically within the fitting routine. The analysis procedure was as follows: The value of z at room temperature was determined by fitting the corresponding conventional spectrum with expression (2). This value was later used as a constraint for the analysis of the MTS. T_C was determined from Fig. 2, and then the three scans of Fig. 3 were fitted simultaneously, β, B_0, A, C, $I_0 e^{-\mu x}$, I_1, Γ_a, z_0 and α_z being the fitting parameters. The Doppler velocities were allowed to vary but they remained at the nominal values within the experimental error. Parameters $T_C = 379.7$ K, $f_s = 0.78$, $\Gamma_s = 0.095$ mm/s were kept fixed. Fig. 5 shows the $B(T)$ curve resulting from the fit (continuous line). For comparison, discrete values of B obtained from the spectra of Fig. 1 and from Ref. [10] are included, the agreement between the three data sets being apparent. In Fig. 5 the values of the parameters of expres-

sion (4) obtained from the fit are also shown. The full curve shown in Fig. 2 is a fit of this thermal scan using the parameters obtained from the other three scans; only v and z were allowed to vary. In this case it is interesting to note that the theoretical curve reproduces well the experimental data not only below T_C but also above it, where the only important parameters are the second-order Doppler effect and the Mössbauer–Lamb factor of the absorber.

In summary, we have shown that MTS is a valuable technique for the determination of the behaviour of the magnetic hyperfine field with temperature. We estimate that required times are an order of magnitude smaller than those demanded by the conventional methodology. An additional advantage is that B is measured as a quasi-continuous function of temperature. In the present work we have applied the method to the simplest case, i.e., a symmetric sextet collapsing into a singlet. More complex situations must be explored both experimentally and theoretically. The MTS approach, along with a closely related method which could be referred to as isothermal scan (time-dependent), have other interesting potential applications not fully explored yet. Among these we can mention the study of structural phase transitions, relaxation processes, amorphous crystallization and solid–solid and solid–gas reaction kinetics. Furthermore, the technique may be improved by expanding the constant velocity procedure to one where the Doppler velocity is changed as a function of temperature, either following a predesigned protocol or as a response to the experiment history. One example of the last case would be the continuous monitoring of the temperature dependence of a Mössbauer transition energy (for instance, as a consequence of the evolution of V_{ij} or B with T). We are currently working on all these subjects [11].

Acknowledgements

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