129I-MÖSSBAUER STUDY OF DIFFUSION EFFECTS IN THE SUPERIONIC CONDUCTOR Ag₃SI

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The superionic conductor Ag₃SI was studied by 129I-Mössbauer spectroscopy in the rhombohedral γ-phase and in the cubic β-phase at temperatures between 4.2 K and 180 K. In the low-temperature γ-phase, one observes well below the γ-β phase transition at 157 K a motional-narrowing-like decrease of the electric-quadrupole interaction, roughly linear with temperature, which points to a diffusional motion of the Ag⁺ ions already in the γ-phase. Diffusional effects are also reflected by an anomalous decrease of the f-factor in the same temperature region, which originates from a restricted short-range diffusional displacement of the iodide ions induced by the hopping Ag⁺ ions.

1. Introduction

We report in this paper preliminary results of a ¹²⁹I-Mössbauer spectroscopic study of diffusion processes in the crystalline superionic conductor Ag₃SI over the temperature range 4.2 K to 180 K.

Mössbauer spectroscopy can be used to obtain information about atomic motions in solids on an atomic scale. In general, there are two different situations for mobile species: localized hopping via available sites in a restricted region of the lattice and long-range macroscopic diffusion. In the latter case one can observe the broadening of the Mössbauer resonance due to diffusion jumps. Broadening becomes detectable if the reciprocal of the jump frequency, 1/νⱼ = τⱼ, is of the order of the nuclear lifetime, τₙ. Singwi and Sjölander [1] and Chudley and Elliott [2] found that the line broadening, ΔW, is inversely proportional to τⱼ, the mean time of residence of the Mössbauer atoms between successive jumps. For purely random jumps in polycrystals, where all possible jump directions are averaged, the Mössbauer line broadening should be proportional to the macroscopic diffusion coefficient D

\[ D = \left( \frac{R^2}{12 \hbar} \right) \left( \frac{f_T}{f_M} \right) \Delta W \] (1)

where R is the jump distance, f_T and f_M the tracer and Mössbauer correlation factor, respectively. Heiming et al. [3] found recently excellent agreement between Mössbauer and tracer diffusion coefficients in pure iron at high temperatures.
The observation of space-restricted diffusion of Mössbauer atoms in a “cage” has been reported in a number of cases, e.g., for interstitially diffusing $^{57}$Fe in Al and Zr [4,5] or hydrogen-loaded alloys [6,7], biomolecules [8,9] and polymers [10]. Such a localized hopping leads to an unbrodened (elastic) line in the Mössbauer spectrum whose intensity reflects the size of the cage, and one or more strongly broadened (quasielastic) lines. The elastic line intensity can be characterized by a fraction of total resonance, $f_e$. The remainder, $1-f_e$, forms the quasielastic line. The temperature dependence of the broadening reflects the hopping frequencies. The width of the quasielastic line, $W$, is roughly given by

$$W = W_0 + a h / t_r$$

where $W_0 = h / \tau_n$ is the natural linewidth and $t_r$ is the mean residence time of the hopping atom. The constant $a$, as well as the exact shape of the quasielastic line depends on details of the hopping geometry [11]. When cage diffusion is very slow at low temperatures ($t_r \gg \tau_n$), the quasielastic line cannot be distinguished from the truly elastic one; in the high-temperature limit ($t_r \ll \tau_n$), the quasielastic line becomes so broad that it can no longer be distinguished from the non-resonant background. Thus, the area under the observable Mössbauer pattern decreases from a low-temperature value, which is proportional to the normal Lamb-Mössbauer factor, $f_{\text{vib}}(T)$, arising from lattice vibrations, to a high-temperature value, which is proportional to $f_e \times f_{\text{vib}}(T)$. In the intermediate region ($t_r = \tau_n$), the quasielastic line will broaden with increasing temperature and hence gradually escape observation. The resulting smooth transition of the observed line intensity from the low-temperature to the high-temperature limit can be described by a temperature-dependent effective $f$-factor, $f_{\text{eff}}(T)$. The exact shape of this transition depends not only on the dynamics and geometry of the hopping of the mobile species, but also on the velocity scale scanned in the Mössbauer experiments. An anomalous temperature dependence of $f_{\text{eff}}(T)$ can be accompanied by a drastic decrease of the quadrupole interaction in the intermediate temperature range [5,12].

Pasternak [13,14] was the first to investigate microscopic features of the self-diffusion mechanism in the classical crystalline solid electrolyte RbAg$_4$I$_5$ by using iodine Mössbauer spectroscopy. He found in complex quadrupole-split $^{129}$I-Mössbauer spectra an additional single line, whose existence was attributed to a fast fluctuating electric-field gradient due to local hopping of the Ag$^+$ ions. The intensity of this line increases exponentially with temperature in the superionic $\beta$-RbAg$_4$I$_5$ phase at temperatures above 120 K.

We have chosen for our measurements Ag$_3$SI, another highly conducting solid electrolyte discovered by Reuter and Hardel [15], which has a much simpler crystalline structure than that of the $\gamma$- and $\beta$-phases of RbAg$_4$I$_5$ with five different iodide sites. Ag$_3$SI exhibits at 157 K a phase transition between the low-temperature $\gamma$-phase and the room-temperature $\beta$-phase. The $\beta$-phase is stable up to the well-known $\beta$–$\alpha$ transition at 519 K [15–17]. The structure of