# Impurity-induced local disorder in the ordered state of the superionic conductor $\beta$-Ag$_2$Se

M. Pasternak,* N. Benczer-Koller, T. Yang, and R. Ruel
*Department of Physics and Astronomy, Rutgers University, New Brunswick, New Jersey 08903*

R. H. Herber
*Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903*
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Mössbauer studies of [119]Sn impurities dissolved in the superionic conductor Ag$_2$Se show a dramatic decrease in the resonance absorption intensity 56 K below the normal superionic transition temperature $T_c = 406$ K. This effect is found to be independent of impurity concentration (0.5–2 at. %) and is reversible with temperature. A mechanism is suggested which relates this new phenomenon to the onset of a local order-disorder phase transition brought about by the fast hopping of Ag$^+$ ions surrounding the impurity Sn atom. Differential thermal analysis of the same samples showed that this "local melting" does not affect the transition temperature of the bulk. The present observations demonstrate that local disorder induced by the Sn impurity coexists with the bulk ordered phase far below $T_c$.

## INTRODUCTION

Superionic materials have been the focus of detailed study in the past few years partly because of the interest in the fundamental interactions leading to long-range ionic diffusion and partly because of their potential use in technology. Numerous studies have tried to elucidate the possible mechanism responsible for the onset of long-range collective ionic diffusion and many of these have focused on the properties of the solid electrolytes of the AgI type.[1] This class of superionic conductors is characterized by a sharp first-order transition from an ordered "normal" ionic crystal to a structure in which the sites occupied by cations are disordered and which has an ionic conductivity comparable to that of liquid electrolytes, several orders of magnitude larger than that of the normal phase. Existing "structural models"[2-5] postulate that the new crystallographic structure drives the material into the conducting phase by opening paths for long-range diffusion. In particular, Rice, Strässler, and Toombs[6] showed that the transition can be stimulated by the interaction of interstitial cation defects with the strain field they induce. An important conclusion of their model is that anomalous large free volumes of cation interstitials should exist *below* $T_c$ in order for the ordered state material to become superionic.

In the present paper we report the observation of local disordered centers induced by the introduction of a heterovalent impurity in the ordered, nonconducting phase of a superionic material. The coexistence of the macroscopic ordered state and impurity-induced disordered cation states was detected by means of Mössbauer spectroscopy on [119]Sn solutes in $\beta$-Ag$_2$Se at temperatures far below $T_c$. As will be shown, the observation is in qualitative agreement with the formulation of Rice et al.[6]

## EXPERIMENT AND DATA

Silver selenide belongs to the AgI type of superionic conductors. At low temperatures the Ag$^+$ cations are ordered.[7] At $T_c = 406$ K, the Se sublattice undergoes a transition from an orthorhombic arrangement into a regular body-centered-cubic array with the interstices only partially occupied by Ag$^+$ ions. Simultaneously, the ionic conductivity increases by four orders of magnitude.[8] A dramatic change is observed in the specific heat[7] with an entropy change equivalent to that occurring at the melting temperature. Similar marked discontinuities at $T_c$ are exhibited by all other thermodynamic properties.[8-12]

In the present study samples of Ag$_2$Se were prepared from the elements in the desired stoichiometric proportions and were doped with 0.5, 1, 2, 3, and 5 at. % of [119]Sn (84% enrichment). The mix was heated in an evacuated quartz tube at 1240 K for 24 h. The resulting material was polycrystalline and its structure was confirmed from room-temperature x-ray powder patterns. Differential thermal analysis of the pure Ag$_2$Se and the samples doped with 0.5, 1, and 2 at. % Sn not only verified the transition temperature of $T_c = 406 \pm 2$ K, but

also showed that $T_c$ is unaffected by the presence of the impurity Sn atoms. Absorbers for the Mössbauer absorption experiments were prepared by mixing and compressing into an aluminum capsule appropriate amounts of finely ground $Ag_2Se(Sn)$ powder and boron nitride dispersant. Measurements were performed in the temperature range $100 \leq T \leq 450$ K with a $Ba^{119}Sn^m O_3$ source at room temperature.

The data obtained for the samples with 0.5, 1, and 2 at.% Sn exhibited a single absorption line with an isomer shift relative to $SnO_2$ of $\delta(300$ K$)$ $=1.53\pm0.10$ mm/sec and a total linewidth at high temperature of $0.91\pm0.01$ mm/sec. The source linewidth was $\Gamma_s=0.50\pm0.02$ mm/sec. Hence the resulting absorber linewidth becomes $\Gamma(300$ K$)$ $=0.41\pm0.02$ mm/sec, which corresponds to an intrinsic broadening of $\Delta\Gamma\approx0.09$ mm/sec. The presence of a single, relatively narrow line, and the lack of quadrupole hyperfine interaction suggest that the Sn impurity occupies a unique lattice site of high symmetry. The value of the isomer shift at 300 K is characteristic of the metal atom in a $4+$ charge state.

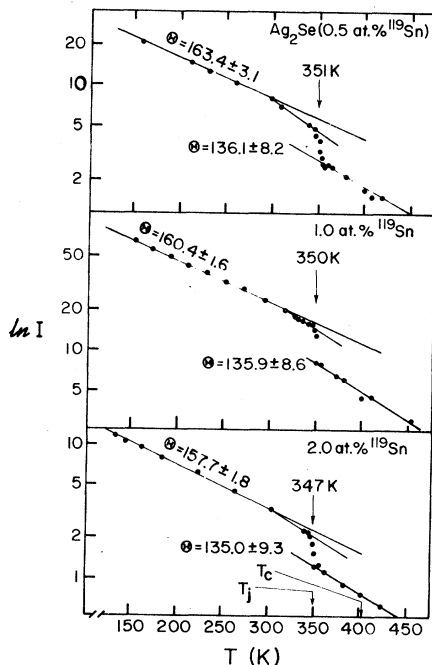Samples with higher Sn concentrations (3 and 5 at.%) gave rise to complex absorption spectra whose
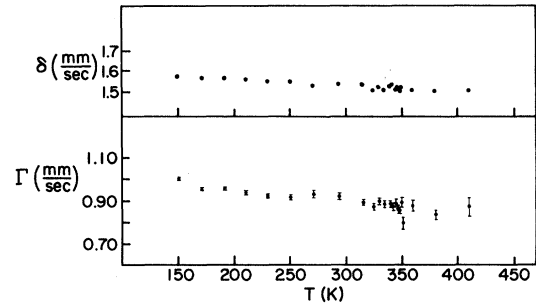


FIG. 2. Temperature dependence of the isomer shift $\delta$ and linewidth $\Gamma$ for the $Ag_2Se$ sample doped with (0.5-at.% $^{119}Sn$. No discontinuity is evident at either $T_j$ or $T_c$.

parameters showed no evidence of discontinuity at $T_c$ or elsewhere. These have not been considered further in the present study.

The temperature dependence of the intensity $I$ of the absorption line is shown in Fig. 1. The absorption intensity undergoes a small discontinuity at $\sim300$ K and a dramatic drop by almost a factor of 2 at $T_j=350$ K. No discontinuity, however, is detected at $T_c$, though the specific heat measurements did exhibit a peak at 406 K for all samples. No discontinuities were observed in the isomer shift or linewidth throughout the whole temperature range (Fig. 2).

## DISCUSSION

The intensity of the absorption line in thin absorbers is proportional to the recoil-free fraction $f$. In the harmonic approximation $f=\exp(-k^2\langle x^2\rangle)$, where $k=12.1$ Å$^{-1}$ is the 23.8-keV $^{119}Sn$ $\gamma$-ray wave number and $\langle x^2\rangle$ is the atomic mean-square displacement. In the high-temperature limit $(T\gg\frac{1}{2}\Theta_D)$, the Debye model predicts a linear dependence of $\langle x^2\rangle$ on $T$, $k^2\langle x^2\rangle$ $=-6E_R T/k_B\Theta_D^2$, where $E_R$ is the recoil energy of the $^{119}Sn$ atom and $k_B$ is Boltzmann's constant. The following features stand out from the data (Fig. 1). (a) At low temperature the data are characterized by a mean-square displacement $\langle x^2\rangle$ linear in $T$, and an average effective Debye temperature $\Theta_D=160\pm1$ K, lower than that reported for pure $SnSe_2$ $(\Theta_D=185$ K$)$.[13] (b) The slope of $\ln I$ changes significantly in the temperature range $300\leq T\leq350$ K corresponding to an appreciable increase in $\langle x^2\rangle$ for the metal atom in this regime, and a correspondingly lower Debye temperature $\Theta_d\approx135$ K. (c) The intensity drops by a factor of 2 at $T_j=350\pm4$ K. (d) The mean-squared displacement at still higher temperatures is again linear in temperature with an effective Debye temperature $\Theta_D=136\pm5$ K, similar to that observed in the (150—300)-K range. (e) A



FIG. 1. Temperature dependence of the resonance absorption line intensity for different concentrations of Sn dopant in $Ag_2Se$. $T_c=406$ K is the transition temperature at which the pure material becomes superionic. $T_j=350\pm4$ K is the temperature at which a marked discontinuity in the Sn resonant absorption occurs.
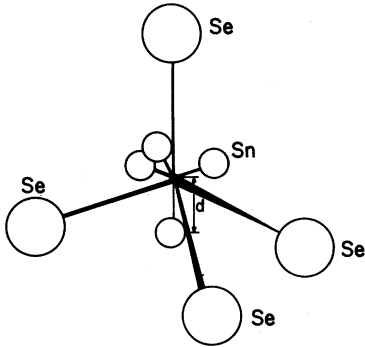
FIG. 3. Crystalline arrangement of the four possible Sn sites within the tetrahedral Se structure.

very slight drop in the transition temperature $T_j$ is observed with increased concentration of $^{119}$Sn. These measurements were reversible without hysteresis.

The observed temperature dependence of the Mössbauer parameters can be understood on the basis of the following model. The tin impurity, due to its high charge state, has a smaller diameter than the neighboring $Ag^+$ cations. The isomer shift is

very close to that of $SnSe_2$ (Ref. 13) $[\delta(78 \text{ K}) = 1.40$ mm/sec] and of $SnI_4$ (Ref. 14) $[\delta(78-180 \text{ K}) = 1.55$ mm/sec], suggesting a cluster formation with tetrahedral symmetry around the Sn impurity with the Se at the vertices (Fig. 3). The contracted Sn-Se distance, which is approximately 0.5 Å per bond shorter than the Ag–Se bond length, results in a larger effective volume, both for the interstitials and the vacancies around the cluster; this substantial increase in the nearest-neighbor volume induced by the $Sn^{4+}$ impurity drives the surrounding $Ag^+$ ions to diffuse. The local diffusion of the $Ag^+$ ions in turn activates a hopping process for Sn ions, among the equivalent sites in the center of the presumed tetrahedral structure (Fig. 2). The onset of vibrations is spontaneous and their frequencies are higher than the value of the reciprocal of the mean life of the 23.8-keV $^{119}$Sn level $(\tau_N = 17.75 \times 10^{-9}$ sec).

Following the Singwi-Sjölander[15] formulation of the Mössbauer spectrum of diffusing ions and the special adaptation of Vogl et al.[16] to the case of discrete jumps into a finite number of sites, the cross section $\sigma(\omega, k)$ for absorption of a photon quantum with energy $E_0 + \hbar\omega$ and momentum $\hbar k$ is given by

$$\sigma(\omega,k) = f_T \sigma_0 \int_{-\infty}^{+\infty} dt \exp(-i\omega t - \Gamma |t| /2\hbar \sum_{m,n=1}^{N} \exp[i\vec{k} \cdot (\vec{R}_m - \vec{R}_n) G_s(\vec{R}_m, t | \vec{R}_n, 0)] , \tag{1}$$

where $\Gamma$ is the natural width of the excited state, $\vec{R}_m$ and $\vec{R}_n$ are the impurity positions (up to $N$), $G_s$ is the self-correlation function of the jump process,[17] $f_T$ is the recoil-free fraction due to thermal vibrations, and $\sigma_0$ is the maximum cross section at $E_0$ (the energy of the excited state). In the limit of fast relaxation, with many jumps within $\tau_N$, the probability of finding the atom at any of the possible $N$ sites is $1/N$ and is independent of $T$. In such a case Eq. (1) may be separated into a time-dependent and a geometrical part, resulting in an unbroadened resonance line, the intensity of which is reduced by a factor $f_j$:

$$\sigma(\omega, \vec{k}) = f_T \sigma_0 L(\omega) f_j(\vec{k}) . \tag{2}$$

$L(\omega)$ represents the unbroadened Lorentzian-shape function and $f_j$ can be written as[17]

$$f_j = \left| \frac{1}{N} \sum_{n=1}^{N} \exp(i\vec{k} \cdot \vec{R}_n) \right|^2 . \tag{3}$$

$f_j$ can be viewed as the summation of the amplitudes of $N$ coherent absorbers at $N$ equivalent positions with phases which depend on $\vec{k}$. In the present case, assuming $N = 4$, and for a polycrystalline absorber, an expression for $f_j$ is obtained by averaging over all directions: $f_j = [2 \sin(kd)/kd]^2$,

where $d$ is the average jumping distance from the center of the tetrahedron (Fig. 3). The experimentally observed factor-of-2 drop in intensity at $T_j$ yields $f_j = 0.5$, from which $d = 0.18$ Å results. This value is considerably smaller than the $Sn^{4+}$-$Se^{2-}$ characteristic distance and supports the concept of local hopping of the Sn impurity and not that of long-range diffusion. The change in the slope of $\langle x^2 \rangle$ (Fig. 1) at $\sim 300$ K, preceding $T_j$, suggests a nonharmonic process associated with local phonon softening. This process probably triggers the onset of local $Ag^+$ diffusion at $T \sim T_j$. It should be emphasized that the assumption of tetrahedral symmetry $(N = 4)$ is not crucial. The equilibrium position for the Sn ion, both below and above $T_j$, may not lie exactly at the center of the cluster, as suggested by the observed broadened line at high temperature $(\Delta\Gamma \sim 0.09$ mm/sec). In principle, at a temperature close to $T_j$ a broadening might be observed if the diffusion frequency $\nu_d$ is close to $\tau_N^{-1} = 0.56 \times 10^8$ sec$^{-1}$. The diffusion frequency is governed by an activation-energy process which yields $\nu_d = \nu_0 e^{-U/kT}$, where $\nu_0$ is the attempt frequency $(\sim 10^{12}$ sec$^{-1})$ and $U$ is the activation energy.[17] In order to observe a broadening, $U$ ought to be of the order of $10 k_B T$, which is much too high an energy for this type of local hopping process. In fact, Petry

et al.[17] observe a line broadening close to $T_j$ in a similar process involving $^{57}Co$ hopping in an Al cage. In that case, however, the transition from fixed position to local diffusion occurs at $\sim 17$ K and the observed activation energy was $U \sim 240$ K.

The onset of long-range, collective diffusion by the $Ag^+$ sublattice at $T \geq T_c$ does not affect the thermal vibrations of the Sn impurity and its first nearest neighbors. The induced local diffusion starting at $T_j$ shields the impurity from the macroscopic disorder. The constancy of the isomer shift over the whole temperature range is consistent with the model of local Sn vibrations, since long-range migration would affect the local chemical bond, thus producing a broadening or a shift in the line position.

In summary, we have shown that time-independent Mössbauer coherence phenomena can be used as a probe for detecting local $Ag^+$ hopping and microscopic disorder within the ordered phase of superionic $\beta$-$Ag_2Se$. The presence of a heterovalent impurity with a high-charge state induces a local increase of the surrounding effective volume, allowing the Ag ions to start diffusion at temperatures significantly below $T_c$. This observation is in qualitative agreement with the suggestion of Rice et al.[6] that large activation volumes below $T_c$ are necessary to drive the superionic state.

## ACKNOWLEDGMENTS

*Present address: Department of Physics, Tel Aviv University, Ramat Aviv, Israel.

[1]K. Funke, Prog. Solid State Chem. 17, 345 (1976).

[2]T. M. Hayes, J. B. Boyce, and J. L. Beeby, J. Phys. C 11, 2931 (1978).

[3]Yu. Ya. Gurevich and Yu. I. Karkats, Zh. Eksp. Teor. Fiz. 72, 1845 (1977) [Sov. Phys.—JETP 45, 968 (1978)].

[4]L. Lam and A. Bunde, Z. Phys. B 30, 65 (1978).

[5]B. A. Huberman, Phys. Rev. Lett. 32, 1000 (1974); J. B. Boyce and B. A. Huberman, Phys. Rep. 51, 189 (1979).

[6]M. J. Rice, S. Strässler, and G. A. Toombs, Phys. Rev. Lett. 32, 596 (1974).

[7]T. Sakuma, K. Iida, K. Honma, H. Okazaki, J. Phys. Soc. Jpn. 43, 538 (1977).

[8]S. Mitayani, J. Phys. Soc. Jpn. 15, 1586 (1960).

[9]P. Junod, Helv. Phys. Acta 32, 567 (1959).

[10]W. Jost and P. Kubachewski, Z. Phys. Chem. (Leipzig) 60, 69 (1968).

[11]J. B. Conn and R. C. Taylor, J. Electrochem. Soc. 10, 977 (1960).

[12]V. H. Glazov and N. M. Makhmudova, Izv. Akad. Nauk. SSSR, Neorg. Mater. 6, 1409 (1970) [Inorg. Mater. (USSR) 6, 1240 (1970)].

[13]R. H. Herber, A. E. Smelkinson, M. J. Sienko, and L. F. Schneemeyer, J. Chem. Phys. 68, 3705 (1978).

[14]S. Bukshpan and R. H. Herber, J. Chem. Phys. 46, 3375 (1967).

[15]K. S. Singwi and A. Sjölander, Phys. Rev. 119, 863 (1960).

[16]G. Vogl, W. Mansel, and P. H. Dederich, Phys. Rev. Lett. 36, 1497 (1976).

[17]W. Petry, G. Vogl, and W. Mansel, Phys. Rev. Lett. 45, 1862 (1980).