

Mössbauer study of Brownian motion of FeSnO_3 particles in liquid-crystal N-(*p*-ethoxybenzylidene)-*p*'-butylaniline (EBBA)

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The effects of Brownian motion of small particles of FeSnO_3 in liquid-crystal EBBA on 14.4-keV Fe^{57} and 23.8-keV Sn^{119} Mössbauer spectra in the temperature range 300 – 360 K are reported. Mössbauer spectral lines begin to broaden a few degrees below the solid \rightarrow nematic phase-transition temperature. In the nematic range and in the isotropic liquid region, except very close to the nematic \rightarrow isotropic phase-transition temperature, the line broadening ($\Delta E - \Gamma$) is linearly proportional to T/η . There is an anomalous change in the line broadening at and near the nematic \rightarrow isotropic phase-transition temperature. The area under resonance sharply decreases at the solid \rightarrow nematic phase transition. In the nematic and in the isotropic region, line broadening is associated with decrease in recoilless fraction.

I. INTRODUCTION

Since the early publication of a paper by Singwi and Sjolander¹ who, using the Van Hove² correlation function, derived an explicit relation between the recoilless fraction f , the linewidth ΔE , and the dynamics of atomic motion in gases, liquids, and solids, several attempts have been made to investigate the diffusion broadening of Mössbauer lines in crystalline solids and in liquids. These experiments can be grouped into three categories, namely: (i) study of atomic diffusion in crystalline solids, (ii) study of atomic diffusion in liquids, and (iii) study of Brownian motion of suspended particles in liquids. Janot³ has critically reviewed the published literature on the effect of atomic diffusion in crystalline solids on Mössbauer line shape. These papers refer to the effect of diffusion of Mössbauer probe atoms as an impurity in the lattice,^{4,5} self-diffusion of Mössbauer probe atoms in the lattice,^{6,7} the effect of anisotropic diffusion,^{8,9} the effect of diffusion of interstitial atoms in a lattice in which the Mössbauer probe atoms are at rest at normal lattice sites,¹⁰⁻¹³ etc. These experiments have established the superiority of the Mössbauer technique in studying diffusion and mass transport in crystalline solids over the macroscopic-tracer technique.

The earliest experiments on atomic diffusion in liquids were done by Bunbury *et al.*¹⁴ and Craig and Sutin.¹⁵ In these experiments, they essentially considered the effect of continuous diffusion of the Mössbauer probe on the nuclear γ -ray resonance linewidth. They showed that, in accordance with the prediction of Singwi and Sjolander, line broadening was invariably proportional to T/η , where T is the absolute temperature and η is the viscosity coefficient

of the liquid. Recently Ruby *et al.*^{16,17} carried out a series of experiments on the Mössbauer effect in ferrous ions and tetravalent tin ions dissolved in aqueous solutions, glasses, and supercooled liquids. These experiments not only clarified the apparently anomalous results reported by Dezsi *et al.*¹⁸ and by Nozik and Kaplan,¹⁹ but also brought out the fact that as the glasses are heated above the glass transition, the mean-square displacement of the Mössbauer probe atoms increases considerably, causing an increase in the linewidth and a decrease in the area under the resonance and in the quadrupole splitting. The decrease in the quadrupole interaction associated with the diffusive broadening, suggested the possibility of the relaxation of the electric-field gradient (EFG). Dattagupta²⁰ analyzed this problem in its various aspects. He considered a situation in which the Mössbauer probe, during the process of diffusion, jumps from one site to another at a certain rate and at the end of each jump sees a different EFG direction. The atomic diffusion and the relaxation of the EFG direction would both cause broadening of the two lines of the quadrupole pattern. However, as the rate of diffusion increases, the relaxation of the EFG will give rise to a shift of the lines towards the center of the pattern. In a later paper, Dattagupta²¹ considered a more general situation in which he investigated the effect of the correlated translational and rotational diffusion of the Mössbauer probe, the latter causing a change in the EFG. Recent experiments of Ruby, Zabransky, and Flinn¹⁶ show that rotational diffusion is not ever likely to be observed by quadrupolar relaxation. In all these experiments, the effect of atomic diffusion on the line shape and the area under the resonance has been considered.

Arguing that the laws of particle diffusion in

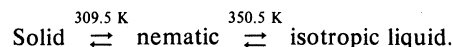
suspension (Brownian motion) in a liquid are the same as those of atomic and molecular diffusion, Bonchev *et al.*²² investigated the effect of Brownian motion of suspended particles on the Mössbauer line shape. Unlike atomic diffusion, one is concerned here with the diffusion of a large particle in a liquid. Bonchev *et al.* found that under certain conditions line broadening varied linearly with T , whereas under certain other conditions they found that the line broadening is proportional to $T^{1/2}$. Bhide *et al.*²³ discussed the effect of atomic and molecular translation and particle diffusion on the Mössbauer line shape. They showed that the line shape and the line broadening are dependent upon the value of the characteristic time $\beta^{-1} = m/6\pi\eta a$ and the value of $\alpha = K^2 D/\beta$, where \vec{K} is the γ -ray wave vector, D is the diffusion coefficient, and m and a are the mass and the radius of the diffusing particle, respectively. They showed that when we have $\alpha \ll 1$, thereby satisfying the space-resolution condition and $\beta^{-1} \ll \tau$, where τ is the lifetime of the nucleus in the excited state, the Mössbauer line is a Lorentzian with a width equal to $2\hbar K^2 D$, in accordance with the prediction of Singwi and Sjolander. When $\alpha < 1$ and $\beta^{-1} \sim \tau$, the Mössbauer line is again a Lorentzian with a width less than that predicted by Singwi and Sjolander. However, when $\alpha > 1$, the line is no longer a Lorentzian, but is a Gaussian with a width proportional to $T^{1/2}$. Recently, Gunther and Wilcox²⁴ generalized the approach to take into consideration the effect of the rotation of the particles. The rotational diffusion is shown to cause a change in the translational velocity.

Comparatively few studies²⁵⁻²⁷ have been reported on the effect of the Brownian motion of suspended particles in a liquid on Mössbauer spectra. In this paper we report our studies on the effect of the Brownian motion of small particles of FeSnO_3 in liquid-crystal EBBA on both ^{57}Fe and ^{119}Sn Mössbauer lines. Since liquid crystals are mesophases in between a crystalline solid and an isotropic liquid, the viscosity of liquid crystals varies over a wide range within a relatively small temperature range. Further, at the isotropic \rightarrow nematic phase transition, orientational order sets in; this is associated with anisotropic effects. Liquid crystals therefore constitute a good medium for investigating the effect of (i) Brownian motion over a considerably broad range of β^{-1} , (ii) the onset of orientational order, and (iii) the phase transitions solid \rightarrow nematic and nematic \rightarrow isotropic liquid, etc., on Mössbauer spectra. We find that both ^{57}Fe and ^{119}Sn Mössbauer lines begin to broaden a few degrees below the solid \rightarrow nematic phase-transition temperature. In the nematic phase, except for a small temperature interval below the nematic \rightarrow isotropic phase transition, the line broadening is proportional to T/η . In the isotropic phase also the line broadening is proportional to T/η but with a dif-

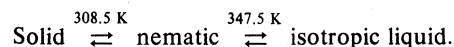
ferent slope. The resonance area is sharply reduced at the solid \rightarrow nematic phase-transition temperature. In both the nematic and the isotropic phases, line broadening is associated with a decrease in recoilless fraction. It is desirable to clarify the difference between the above experiments and those of Detjen and Urich.⁹ They observed ^{57}Fe Mössbauer line broadening for iron-bearing probe molecules, 1, 1'-diacetyl-ferrocene (DAF), in a glassy liquid crystal above the glass-transition temperature when the liquid crystal was aligned so that the γ -ray beam was either along the molecular axis or perpendicular to the molecular axis. They observed that the line broadening was different in the two cases, showing anisotropy of diffusion in a supercooled liquid crystal.

II. EXPERIMENTAL

The liquid crystal chosen for this investigation was N-(*p*-ethoxy-benzylidene)-*p*'-butylaniline (EBBA) which has the following phase transitions:



Liquid-crystal samples were obtained from E. Merck. Composite particles of FeSnO_3 (preparation described in Ref. 23 earlier) enriched to about 85 at.% ^{119}Sn were suspended in the isotropic phase of liquid-crystal EBBA. The compound FeSnO_3 was ground in an agate mortar and was introduced in the isotropic liquid at 350 K. The mixture was centrifuged to remove heavier particles. The suspension was allowed to stay for three days. Only the upper part of the sample was injected into a hermetically sealed disk-shaped absorber cell. Care must be taken to prevent contamination of the sample with moisture. The absorber temperature could be varied from 273 to 400 K. The temperature of the sample could be maintained at the desired value to within ± 0.5 K. On addition of FeSnO_3 particles to the liquid crystal, the phase-transition temperatures were slightly altered. The new phase transitions were



The EBBA coefficient of viscosity was measured using a rotational viscometer model rheostat-2 (VEB MLW, Fruggerate - Werk, Medingen). The temperature of the sample was varied using a water-circulation thermostat model U - 10 (VEB MLW, Fruggerate - Werk, Medingen) and could be controlled to within ± 0.2 K. The coefficient of viscosity was determined by measuring the shear stress and shear strain. Figure 2 shows the variation of the viscosity coefficient with temperature. The differential-scanning-calorimetry (DSC) thermogram of the EBBA phase transitions is also shown in the same figure. Notably, the higher-temperature isotro-

pic phase has a characteristically higher viscosity than the nematic mesophase at the near lower temperature. This is because the mesophase is readily and highly ordered in the direction of flow, thus increasing the flow rate. The nematic \rightarrow isotropic phase transition and the visual clarity of the sample occur at a temperature just below the temperature at which viscosity is maximum.

Mössbauer experiments were performed employing a standard constant-acceleration spectrometer based on an electromechanical feedback system. The data were stored in a 1024-channel ND 100 multichannel analyzer which was operated in a multichannel scaling mode. The spectra were fitted to machine-computed Lorentzians using the least-squares fitting method and an IBM 360/44 computer. The area under the resonance, the isomer shift, and the linewidth were determined from the computer-fitted spectra. The sources used in these studies were ^{57}Co in a Pd matrix and ^{119}Sn in a CaSnO_3 matrix.

III. RESULTS AND DISCUSSIONS

Some of the representative ^{57}Fe and ^{119}Sn Mössbauer spectra at various temperatures are shown in Figs. 1(a) and 1(b). These spectra could be well

fitted to machine-computed Lorentzians. In the solid phase, the spectra in terms of isomer shift and quadrupole splitting correspond closely to those obtained with pure FeSnO_3 compressed powder. In the nematic and isotropic liquid phases, the isomer shift and quadrupole splitting remained unaltered but in these phases the γ -ray resonance lines broadened considerably. This shows that there is no chemical reaction between the suspended particles and the liquid-crystal matrix.

In Figs. 2(a) and 2(b) we plot the diffusive line broadening as a function of temperature for 14.4-keV ^{57}Fe and 23.8-keV ^{119}Sn Mössbauer spectra, respectively. In the solid phase, the linewidth is sensibly constant. The line begins to broaden 2–3 °K below the solid \rightarrow nematic phase-transition temperature. In the nematic phase, the line broadens further. However, in both ^{57}Fe and ^{119}Sn Mössbauer lines, the broadening $\Delta E - \Gamma$ does not vary linearly with temperature T . As the nematic \rightarrow isotropic phase transition is approached, the line broadening decreases, reaches a minimum, and then increases with further increase in temperature. Notably, the higher-temperature isotropic phase has a lower line broadening than the nematic phase at the near lower temperature. As in the case of viscosity variation with

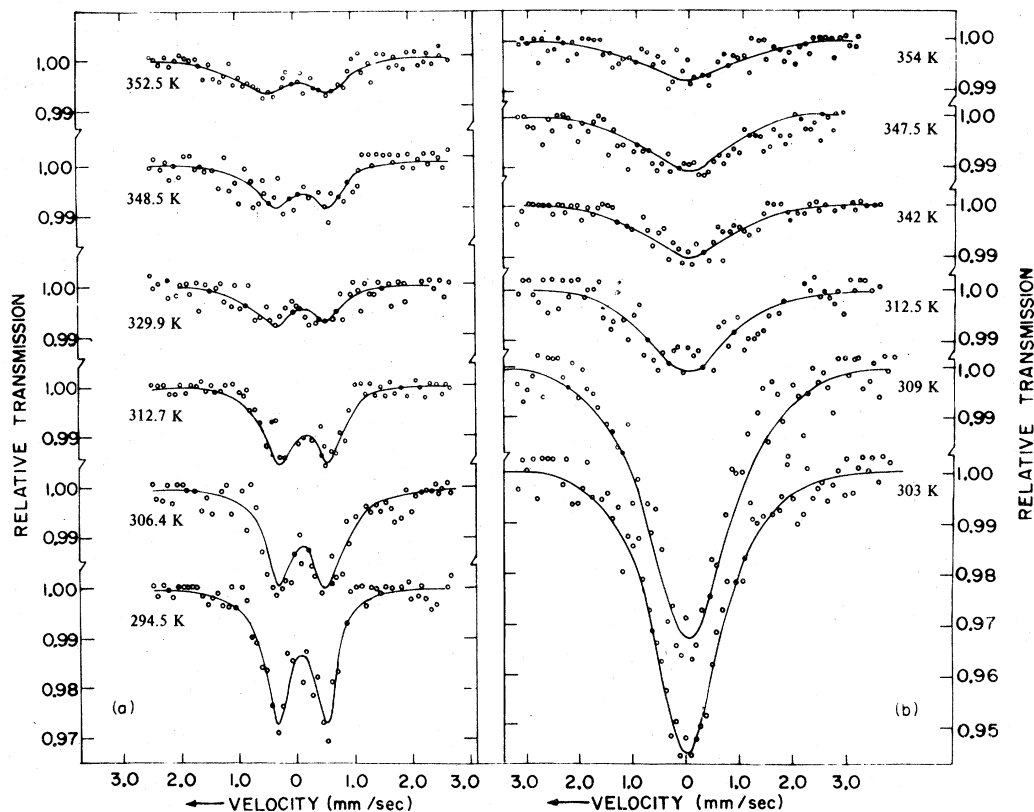


FIG. 1. (a) ^{57}Fe Mössbauer spectra of FeSnO_3 particles in EBBA at various temperatures; Pd: ^{57}Co source. (b) ^{119}Sn Mössbauer spectra of FeSnO_3 particles in EBBA at various temperatures; CaSnO_3 : ^{119}Sn source.

temperature, the nematic \rightarrow isotropic phase transition and the associated visual clarity of the sample occur close to the temperature at which the line broadening is minimum. These changes in the line broadening at and close to the nematic \rightarrow isotropic phase transition, are obviously due to the onset of molecular orientational order at the phase transition. This change is partly due to the viscosity change occurring at the phase transition owing to the ordering effect of the liquid crystal and partly due to the effect of ordering itself on the diffusion of FeSnO_3 particles along the γ -ray wave vector. In order to identify the relative roles played by these two factors, we plot, in Figs. 3(a) and 3(b), the variation of the line broadening $\Delta E - \Gamma$ as a function of T/η . We find that in the nematic range, the line broadening $\Delta E - \Gamma$ is proportional to T/η . The line broadening $\Delta E - \Gamma$ versus temperature curve deviates from linearity at and near both the solid \rightarrow nematic and nematic \rightarrow isotropic transition temperatures. In the isotropic range, the line broadening $\Delta E - \Gamma$ is again proportional to T/η but it varies more steeply in the isotropic phase than in the nematic phase.

From the slope of $\Delta E - \Gamma$ vs T/η in the nematic range, we calculated the diameter of the diffusing particles. From Mössbauer data for ^{57}Fe and ^{119}Sn in the nematic range, we find that the particle diameter is nearly $1.0 \pm 0.2 \mu\text{m}$. Using the slope of $\Delta E - \Gamma$ vs T/η in the isotropic phase we find that the particle diameter is $0.55 \pm 0.2 \mu\text{m}$. For the sake of comparison, we examined the particles with a Philips EM 200 transmission-electron microscope. From the electron micrographs we found that the particle size varied

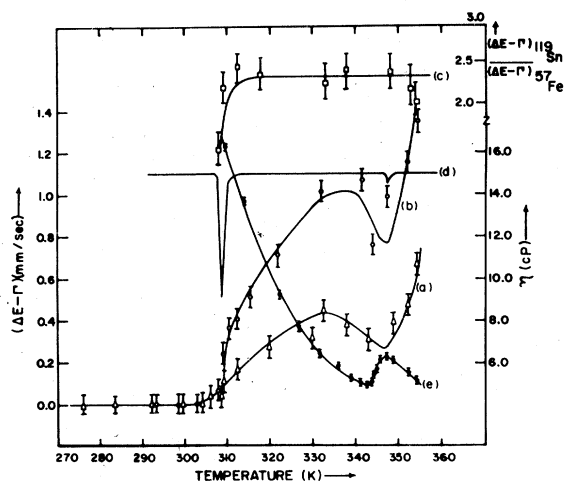


FIG. 2. (a) Variation of ^{57}Fe Mössbauer line broadening $\Delta E - \Gamma$ with temperature. (b) Variation of ^{119}Sn Mössbauer line broadening $\Delta E - \Gamma$ with temperature. (c) Variation of $(\Delta E - \Gamma)_{119\text{Sn}} / (\Delta E - \Gamma)_{57\text{Fe}}$ with temperature. (d) DSC thermogram of EBBA showing the phase transitions. (e) Variation of the viscosity coefficient η (in centipoise) with temperature T .

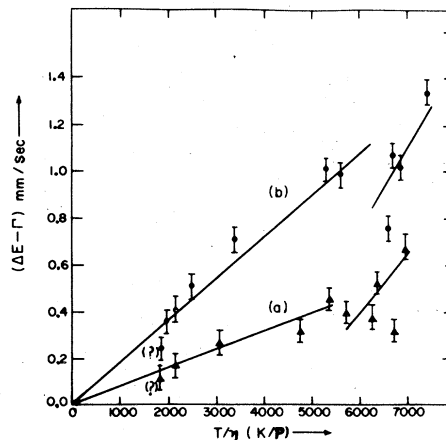


FIG. 3. (a) Variation of ^{57}Fe Mössbauer line broadening $\Delta E - \Gamma$ with T/η . (b) Variation of ^{119}Sn Mössbauer line broadening $\Delta E - \Gamma$ with T/η .

between 0.4 and $0.8 \mu\text{m}$. In order to elucidate the difference in particle size as determined from the data in the nematic and in the isotropic liquid phases, we plot the variation of $D = (\Delta E - \Gamma) / 2\hbar K^2$ with $1000/T$ in Fig. 4. The temperature dependence of the diffusion is roughly Arrhenius-like. However, the activation energy is different in the nematic (0.58 eV) and in the isotropic liquid phase (0.87 eV), as it is greater in the isotropic liquid phase. The higher activation energy in the isotropic liquid is understandable in the long-chain organic compound EBBA.

Quantitatively it is difficult at this stage to comment on the discrepancy in particle size as determined from the nematic and the isotropic phase data, and the electron micrograph data. These differences may be due to several possible reasons. First, the

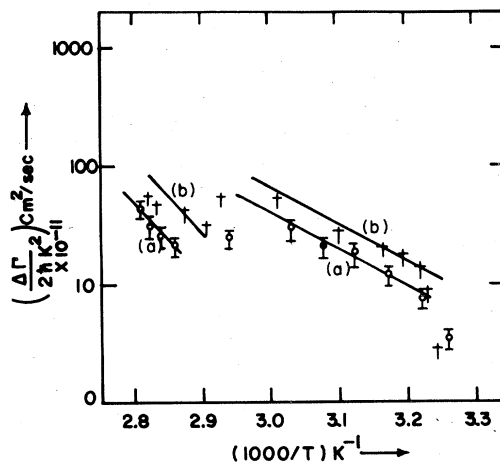


FIG. 4. (a) Variation of the diffusion coefficient $D = (\Delta E - \Gamma) / 2\hbar K^2$ with $1000/T$ for ^{57}Fe Mössbauer spectra. (b) Variation of the diffusion coefficient $D = (\Delta E - \Gamma) / 2\hbar K^2$ with $1000/T$ for ^{119}Sn Mössbauer spectra.

particles are not of uniform size. Second, in the nematic phase the viscosity coefficient is anisotropic and it is not rigorously correct to use the value of η determined using a viscometer to compute the line broadening. Detailed investigations on aligned nematic liquid crystals, using accurately measured and uniformly sized particles, made by employing a newly developed cryochemical technique,²⁸ are under progress.

Assuming that the line broadening is given by $\Delta E - \Gamma = 2\hbar K^2 D$ we find that $(\Delta E - \Gamma)_{^{119}\text{Sn}} / (\Delta E - \Gamma)_{^{57}\text{Fe}}$ should be independent of temperature and should be equal to $K_{^{119}\text{Sn}}^2 / K_{^{57}\text{Fe}}^2$. In Fig. 2(c) we plot $(\Delta E - \Gamma)_{^{119}\text{Sn}} / (\Delta E - \Gamma)_{^{57}\text{Fe}}$ as a function of temperature. We find that although this ratio is independent of temperature, it is equal to 2.35 as against the expected value of 2.67.

Significantly, the quadrupole interaction is seen to be independent of temperature over the temperature range studied. This indicates that quadrupole relaxation has relatively a little role to play in line broadening.

Simultaneously, with the broadening of the Mössbauer lines, we observed a reduction in the area under resonance and thus in the f factor. In Fig. 5 we plot the log of the area under resonance as a function of temperature. In the solid phase log A decreases with temperature in much the same way as in any other solid. A decrease in log A with temperature faster for ¹¹⁹Sn Mössbauer lines than for ⁵⁷Fe Mössbauer lines is indeed expected. At the solid \rightarrow nematic phase-transition temperature, log A decreases rather abruptly and considerably, the decrease being much greater for ¹¹⁹Sn than for ⁵⁷Fe Mössbauer lines. It is significant to note that there is no such abrupt change in the broadening of the Mössbauer lines across this phase transition. In both the nematic and isotropic phases, the line broadening is associated with a corresponding decrease in the area under the resonance.

Unlike atomic and molecular diffusion, we are concerned here with the diffusion of a relatively large particle. The f factor in this situation is contributed by a product of two factors, f_1 and f_2 , the factor f_1 arising out of the mean-square displacement $\langle X_L^2 \rangle$ of the Mössbauer nucleus within the particle relative to the center of mass of the particle. The factor f_2 arises out of the mean-square displacement of the center of mass (particle as a whole) $\langle X_B^2 \rangle$ of the particle. Over the temperature range studied $\langle X_L^2 \rangle$ is not expected to change considerably and indeed the effects of phase change and diffusion broadening are reflected in the f factor through the changes in $\langle X_B^2 \rangle$. At the solid \rightarrow nematic phase-transition temperature, we observed a large change in the f factor without a corresponding change in the line broadening. The decrease in the area under the resonance at the

phase-transition temperature is obviously due to the softening of the host matrix. Ruby, Zabransky, and Flinn¹⁶ observed a large change in the f factor at the glass-transition temperature T_g as the glass transformed into a supercooled liquid. They have attributed this change in the f factor to the possibility of some of the continuum modes below T_g going soft above T_g and reappearing at lower frequencies. Lacking knowledge of the dynamical behavior of a large particle in a liquid-crystal matrix, it is difficult to explain quantitatively the observed change in the present case. However, it is certain that the decrease in the f factor at the phase transition is essentially due to the softening of the lattice.

In the nematic and isotropic liquid phases, the decrease in the area under the resonance can be correlated satisfactorily with the diffusion broadening. Indeed it can be shown that log A will decrease linearly with T with a slope equal to $K_\beta \tau / 6\pi\eta a \chi^2$, where K_β is the Boltzmann constant. It is obvious that log A vs T will be a faster falling function in the case of ¹¹⁹Sn than in that of ⁵⁷Fe. Extending these arguments one can show that log A will vary linearly with the line broadening $\Delta E - \Gamma$. Jenson²⁹ and Ruby *et al.*¹⁶ have shown such a relationship between the f factor and the line broadening.

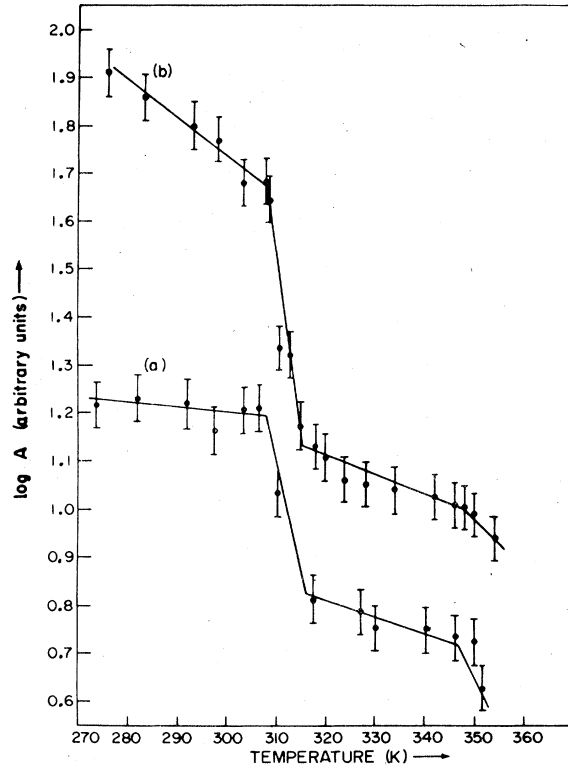


FIG. 5. Plot of log A as a function of temperature for (a) ⁵⁷Fe and (b) ¹¹⁹Sn Mössbauer spectra.

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- ¹K. S. Singwi and A. Sjolander, *Phys. Rev.* **120**, 1093 (1960).
²L. Van Hove, *Phys. Rev.* **95**, 249 (1954).
³Ch. Janot, *J. Phys.* **37**, 253 (1976).
⁴R. C. Knauer and J. G. Mullen, *Phys. Rev.* **174**, 711 (1968).
⁵R. C. Knauer and J. G. Mullen, *Appl. Phys. Lett.* **13**, 150 (1968).
⁶S. J. Lewis and P. A. Flinn, *Appl. Phys. Lett.* **15**, 331 (1969).
⁷S. J. Lewis and P. A. Flinn, *Philos. Mag.* **3**, 977 (1972).
⁸H. Pollak, M. De Coster, and S. Amelinck, *Proceedings of the 2nd International Conference on the Mössbauer Effect*, edited by H. Pollack, M. DeCoster, and S. Amelinck (Wiley, New York, 1962).
⁹R. E. Detjen and D. L. Uhrich, in *Mössbauer Effect Methodology*, edited by I. J. Gruvermann (Plenum, New York, 1974), Vol. 9, p. 113.
¹⁰G. M. Hood, *Philos. Mag.* **21**, 305 (1970).
¹¹K. Sorenson and G. Trumphy, *Phys. Rev. B* **7**, 1791 (1973).
¹²M. A. Krivoglaз and S. P. Repetskii, *Sov. Phys. Solid State* **8**, 2325, (1967).
¹³J. P. Motte, A. El Maslout, and N. N. Greenwood, *J. Phys. (Paris)* **35**, C6 - 507 (1974).
¹⁴D. St. P. Bunbury, J. A. Elliott, H. E. Hall, and J. M. Williams, *Proc. Phys. Soc. (London)* **77**, 129 (1961); also *Phys. Lett.* **6**, 34 (1963).
¹⁵P. R. Craig and N. Sutin, *Phys. Rev. Lett.* **11**, 460 (1963).
¹⁶S. L. Ruby, J. C. Love, P. A. Flinn, and B. J. Zabransky, *Appl. Phys. Lett.* **27**, 320 (1975).
¹⁷S. L. Ruby and I. Pelah (unpublished).
¹⁸I. Dezsi, L. Keszthelyi, B. Molnar, and L. Pocs, in *Proceedings of the Asilormer Conference*, edited by E. Matthias and D. A. Shirley (North-Holland, Amsterdam, 1968), p. 566.
¹⁹A. Nozik and M. Kaplan, *J. Chem. Phys.* **47**, 2960 (1967); and *Chem. Phys. Lett.* **1**, 391 (1967).
²⁰S. Dattagupta, *Phys. Rev.* **12**, 47 (1975).
²¹S. Dattagupta, *Phys. Rev.* **14**, 1329 (1976).
²²T. Bonchev, P. Aidemirslei, I. Mandzhukov, N. Nedyalkova, B. Skorchev, and A. Strigacher, *Zh. Eksp. Teor. Fiz.* **50**, 62 (1966) [*Sov. Phys. JETP* **23**, 42 (1966)].
²³V. G. Bhide, R. Sundaram, H. C. Bhasin, and T. Bonchev *Phys. Rev. B* **3**, 673 (1971).
²⁴L. Gunther and J. Z. Wilcox, *J. Stat. Phys.* **12**, 205 (1975).
²⁵A. V. Zatovskii, *Ukr. Fiz. Zh. (Russ. Ed.)* **17**, 1809 (1972).
²⁶A. Ya. Dzyznblik, *Zh. Eksp. Teor. Fiz.* **67**, 1534 (1974) [*Sov. Phys. JETP* **40**, 763 (1974)].
²⁷H. Keller *et al.*, *Solid State Commun.* **16**, 253 (1975).
²⁸F. J. Schnettler, F. R. Monforte, and W. W. Rhodes, in *Science of Ceramics*, edited by G. H. Stewart (The British Ceramic Society, 1968), p. 79.
²⁹J. H. Jenson, *Phys. Kondens. Mater.* **13**, 273 (1971).