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Microscopic view of disorder in the ordered phase of superionic $RbAg_4I_5$

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Mössbauer spectroscopy in ^{129}I was employed to verify the existence and investigate the properties of local disorder in the "ordered" state of the superionic conductor $RbAg_4I_5$. Studies were conducted in the temperature range of 4—180 K covering the low-temperature γ phase ($T < 122$ K) and part of the high-conductivity, disordered β phase. The absorption spectra at all temperatures were analyzed with two iodine sites, characterized by their quadrupole splitting and isomer-shift values and a third site with a nonsplit single line. It was found that the electric field gradient (efg) at the ^{129}I nucleus, produced by the neighboring Ag ions, has a continuous linear temperature dependence down to 4.2 K. The hyperfine constants and the Debye-Waller factor showed no discontinuity at T_c. The anomalous existence of the single line has been attributed to a fast fluctuating efg due to local hopping of the Ag ions. This dynamic disorder is present even at low temperatures where (8—10)% of Ag ions are locally hopping, and its occurrence increases drastically at $T > T_c$. A nonharmonic Debye-Waller factor was observed from which a linear temperature-dependent Debye temperature could be derived.

I. INTRODUCTION

The superionic conductors of the AgI class,[1] characterized by cation-disordered phases, exhibit remarkable physical properties. In the conducting phase they can be described as a relatively rigid crystalline framework, composed of the nonconduction anions such as the chalcogenides and iodides, with mobile cations distributed in a statistically disordered way among the many available sites provided by the anion skeleton.[2] Below a critical temperature T_c, following a first-order phase transition the cations become crystallographically ordered, and the conductivity decreases discontinuously by several orders of magnitude, reaching values of normal ionic solids.[2]

An interesting subject, and perhaps crucial to the elucidation of the mechanism behind this unique phase transition, is the nature of the *ordered-phase* preceding the superionic phase. Existing theories of phase transition, such as those of Huberman[3] and Rice, Strassler, and Toombs,[4] do not *a priori* impose any particular configuration requirements on the low-temperature phase. Nevertheless, from the few studies reported on the properties of the low-temperature phase of AgI-class materials [such as CuI (Refs. 5 and 6) and AgI (Ref. 7)], evidence exists for partial configurational disorder in the *ordered* phase. Strong evidence for disorder in the ordered state was reported also for the low-temperature, γ phase of $RbAg_4I_5$, an ionic solid with exceptionally low transition temperature ($T_c = 121.8$ K). Crystallographic studies by Geller[8] concluded that the γ phase down to 90 K is not completely ordered and that it is unlikely that the 121.8 K transition is of first order. Jonston *et al.*[9] reported an excess of specific heat starting from 50 K up to T_c, suggesting a continuous configuration disorder. Data analysis of conductivity under pressure by Allen and Lazarus[10] could be interpreted by assuming partial disorder in the γ phase. Owing to the complex structure of this material, no definite clues could be obtained concerning the nature of this possible partial disorder. Motivated by the importance of this subject, we undertook to investigate the microscopic features of the γ phase and its transition into β-$RbAg_4I_5$ by applying ^{129}I Mössbauer effect (ME) spectroscopy. This is the first report using this method for studies of order-disorder in superionic solids.

II. EXPERIMENTAL

Polycrystalline $RbAg_4I_5$ was prepared by direct reaction of stoichiometric amounts of $Ag\,^{129}I$ and $Rb\,^{129}I$. AgI and RbI were synthesized from precipitates of $AgNO_3$ and $RbCO_3$ in a $H\,^{129}I$ solution. The purity of the AgI and RbI was confirmed by Mössbauer spectroscopy as well as by x-ray analysis. The samples were obtained after heating the ingredients under vacuum to 450 °C. The structure was confirmed by x rays. No residuals of nonreact-

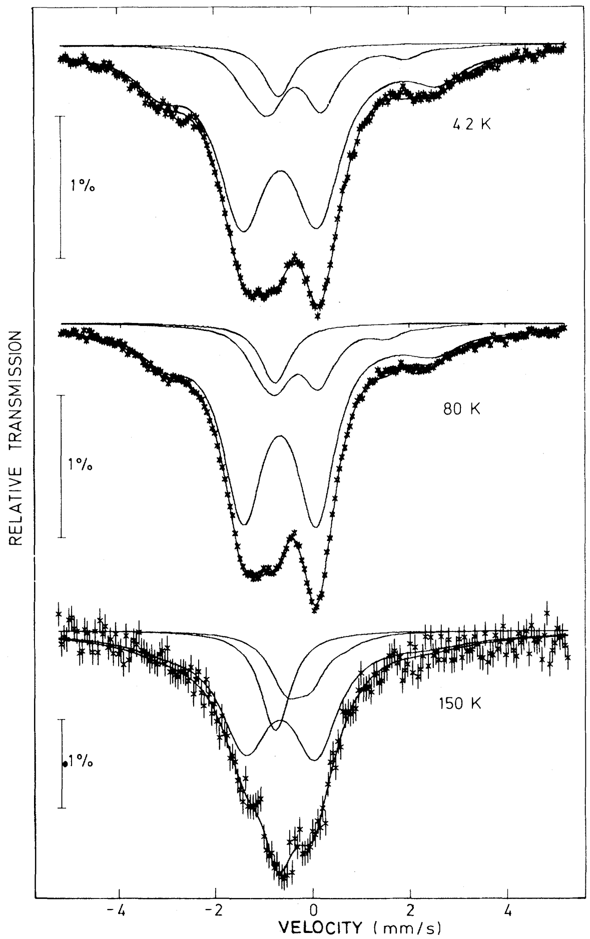

FIG. 1. ^{129}I Mössbauer spectra of $RbAg_4{}^{129}I_5$ at 4.2, 80, and 150 K. Each spectrum is fitted with three components. The least-squares fit is shown by the solid line through the experimental points.

ing AgI and RbI or other phases were found in this analysis. Measurements were performed with two samples produced by the same procedures. To avoid line broadening due to saturation effects, absorbers with various thicknesses were used, namely, 3.8 mg/cm^2 (^{129}I) at the lowest temperature and up to 17 mg/cm^2 at the highest temperature. The source used was $Sn^{129m}Te$, and was kept at liquid-helium temperature. The temperature range of the experiments was between 4.2 and 180 K, the maximum temperature at which a reliable spectrum could still be analyzed. The absorption spectra of $RbAg_4I_5$ at three different temperatures is shown in Fig. 1. The solid line through the experimental points is a result of a least-squares fitting.

III. DISCUSSION

There are two low-temperature transitions of $RbAg_4I_5$, a first-order one ($\gamma\rightarrow\beta$) at 121.8 K and a second-order one ($\beta\rightarrow\alpha$) at 209 K.[8] The β phase is rhombohedral with space group $R32$ (D_3^7), and the γ phase is trigonal, most probably with space group $P321$ (D_3^2). According to Geller the two phases are closely related and the iodide substructure persists. The crystallographic data in the β phase provides for five iodine sites: two with site symmetry 1, two with site symmetry 2, and one with (axial) symmetry 3. The low symmetries of the sites indicate the existence of nonzero electric field gradients (efg) at the ^{129}I nucleus.

The interaction of the efg with the nuclear quadrupole moment induces a quadrupole splitting in the ground ($I=\frac{7}{2}$) and excited ($I=\frac{5}{2}$) states of the 27.8-keV Mössbauer transition in ^{129}I. Thus, the positions ϵ_{ij} of the lines can be expressed as

$$\epsilon_{ij}=(C/E_\gamma)(e^2qQ/4)[(Q^*/Q)C(\tfrac{5}{2},m_j^*)$$
$$-C(\tfrac{7}{2},m_i)] ,$$

where e^2qQ is the quadrupole coupling constant of the ground state, Q^*/Q is the ratio of the excited- to ground-state quadrupole moments, and $C(I,m)$ are functions of the eigenvalues and the asymmetry parameter η of the efg. In the case of axial symmetry, when $\eta=0$,

$$C(I,m)=[3m^2-I(I+1)]/I(2I-1) .$$

A. Spectra analysis

From the crystallographic symmetries one would have predicted a spectra composed of five quadrupole split components, e.g., four with $\eta\neq0$ and one with $\eta=0$. However, due to the intrinsic resolution of the experimental results, this could not be reliably analyzed. Preceding the computer fitting the following features were observed, namely, the presence of a single-line component—particularly emphasized at high temperatures and an intense component with $\eta\neq0$. This last observation is based on the presence of a peak at ~3 mm/s (see Fig. 1). Thus by keeping in mind the symmetry restrictions the following were resolved: (a) a quadrupole-split component (designated as $I1$) with a nonvanishing η value and a Gaussian distribution of efg with δ as its breadth, (b) a quadrupole-split component with $\eta=0$ ($I2$), and (c) an unsplit line ($I3$). A Gaussian distribution was assumed in order to account for the four different I sites with $\eta\neq0$. In the early stages of fitting trials the linewidths of all three components were fixed to the experimental value obtained with a thin CuI single-line absorber. By letting the relative intensities of the components vary freely, it was found for a few temperatures that the intensity ratio of $I1$ to $I2$ was 4:1 within the experimental error. Since this

TABLE I. The values of the isomer shift (IS) with respect to SnTe at 4.2 K, the quadrupole coupling constants (e^2qQ) and corresponding quadrupole frequencies, and the η parameter. The numbers in parentheses correspond to the error in the last figure. All values are for $T = 4.2$ K, where δ, the breadth of the efg distribution of $I1$, is zero (see Fig. 2).

	IS (mm/s)	e^2qQ (mm/s)	ν_Q (MHz)	η
$I1$	$-0.66(1)$	$-12.1(9)$	386(30)	0.68(2)
$I2$	-0.27	$-8.1(2)$	258(5)	
$I3$	$-0.76(3)$			
AgI	$-0.72(1)$			
RbI	$-0.86(1)$			

finding was in accord with the crystallographic data, it was decided to keep it fixed through the whole temperature range. Furthermore it was found that values of the isomer shift of all the three components, $e^2qQ(I1)$, and η are independent of temperature within the experimental error. This implies that there are in fact only four variable parameters for the thirteen spectra recorded with sample 1 and eight with sample 2, namely, $e^2qQ(I2)$, δ, intensity of $I1$ and $I2$ combined, and intensity of $I3$. The quality and consistency of the theoretical spectra at all temperatures were excellent and the hyperfine constants deduced from the fitting at 4.2 K are given in Table I. In Fig. 2 we depict the variation of δ and of $\Delta e^2qQ(I2)$, where

$$\Delta e^2qQ = e^2qQ(T) - e^2qQ(4.2\ \mathrm{K}) ,$$

as a function of temperature. Figure 3 shows the temperature dependence of the relative intensities of $I1$ and $I2$ combined and of $I3$.

B. The electric field gradient

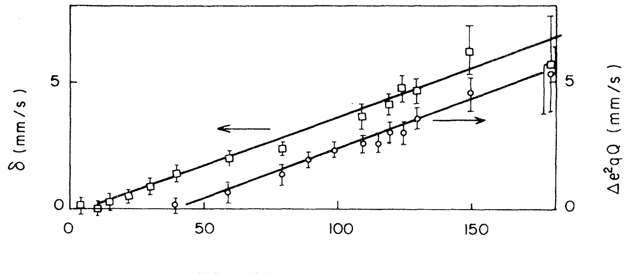

FIG. 2. Temperature dependence of the breadth of the efg, δ, of site 1 (left side) and of Δe^2qQ [$= e^2qQ(T) - e^2qQ(4.2\ \mathrm{K})$] of site 2.

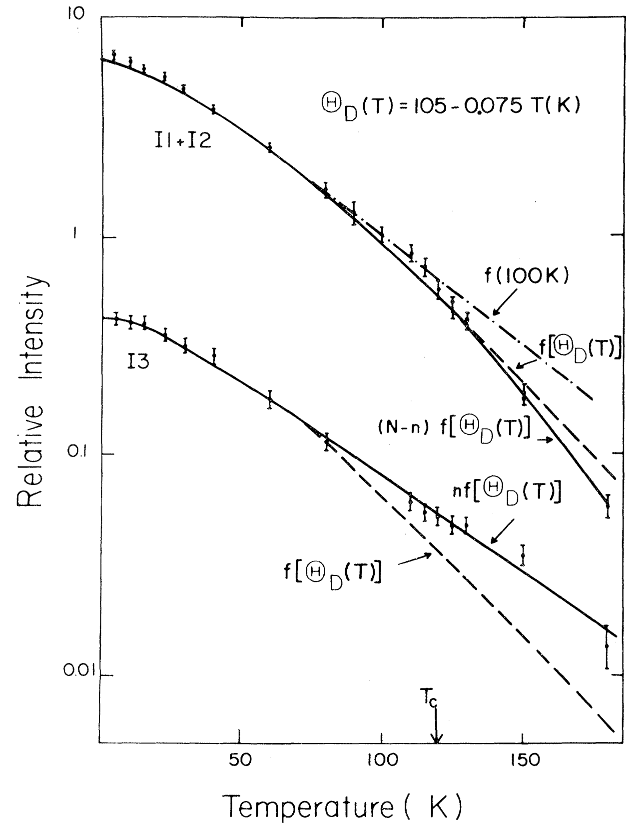

FIG. 3. Relative intensity of the absorption lines of $I1+I2$ combined (upper part) and of $I3$ (lower part). The —·—·—· line corresponds to a fitting of $f(T)$ yielding $\Theta_D = 100$ K. The — — — line corresponds to a theoretical expression for $f(T)$, where Θ_D varies with T, and the solid line combines both $f(T)$ and population variation with T for the $I1+I2$ and $I3$ sites.

In iodide crystals such as $RbAg_4I_5$ we assume that the main contribution to the efg arises from the nonspherical spatial distribution of point charges surrounding the iodine. Thus the components of the efg tensor q_{ij} $(i,j = 1,2,3)$ are directly related to the ions' positions $(x_i x_j)$; namely,

$$q_{ij} = (1-\gamma) \sum_{k}^{n} e_k (3x_{ki}x_{kj} - r_k^2 \delta_{ij}) / r_k^5 , \qquad (1)$$

where $(1-\gamma)$ is the Sternheimer antishielding factor, r_k is the distance of the kth charge e_k from the iodine nucleus, and δ_{ij} is the Kronecker delta. Because q_{ij} varies as r^{-3}, the contribution to the sum in (2) will be primarily from the nearest Ag^+ neighbors. Consequently, the efg measured at an iodine site becomes a direct probe in an atomic scale of disorder around the iodine site. If x_{ij} is temperature dependent so will be the efg.

The unusual temperature dependence of δ and Δe^2qQ, as shown in Fig. 2, is a direct manifestation of a continuous crystallographic disorder. Unfortunately, due to the complexity of the structure it is impossible to deduce from the efg the values of the

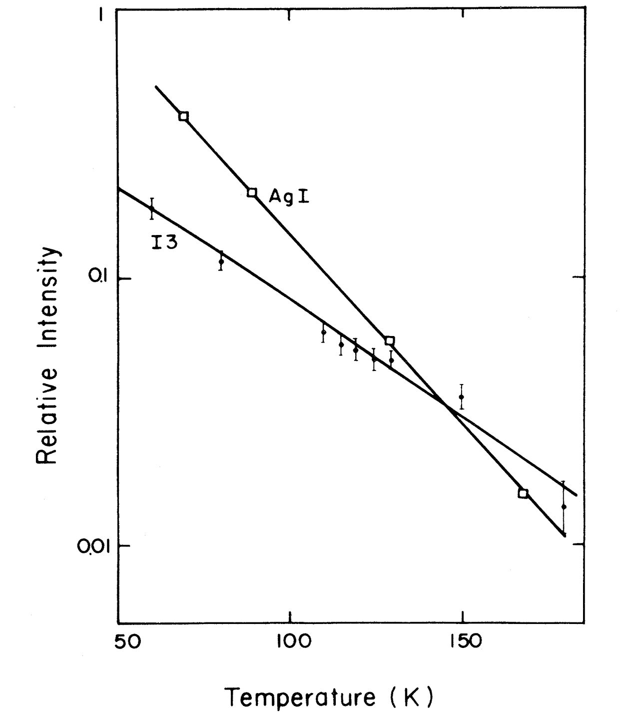

FIG. 4. Temperature dependence of the relative intensity of the absorption peaks of Ag ^{129}I and $I3$ in $RbAg_4I_5$. From the slope of the curve $\Theta_D=82\pm2$ K was derived for AgI. As can be seen the slopes are significantly different for both species.

Ag^+ positions x_{ij}. However, it is interesting to note the following. (1) Both $\delta(T)$ and $e^2qQ(T)$ are linear with T with the same slope. This suggests that they originate from the same mechanism; namely, both parameters are function $\langle 1/r^3\rangle$ which varies in temperature. (2) There is no discontinuity at T_c.

C. The nature of the single-line absorption

The presence of a single-line absorption in a $RbAg_4{}^{129}I_5$ absorber is anachoristic. Crystallographically there are no sites with symmetries higher than $C3$ which will render a zero efg. Thus this spectral component ($I3$) must be due to one of the following reasons: (1) impurities of other Rb-Ag-I phases with iodine sites having cubic symmetry; (2) nonreacting residuals of AgI or RbI, or (3) sites of iodine in $RbAg_4I_5$ with vanishing efg due to time-dependent phenomena such as fast quadrupole relaxation.

The first possibility is ruled out on the basis that only stable compound of Rb-Ag-I mixture, Rb_2AgI_3, is orthorhombic with low-symmetry iodine sites.[11] In the second possibility the most plausible one is AgI, because its isomer shift is quite close to that of $I3$ (see Table I). As mentioned before, no lines of AgI were detected by x-ray diffraction. Still, a possibility exists that very small microcrystals of AgI could result in broad x-ray lines, thus avoiding detection by this method. The ultimate test was to compare the Debye-Waller factor of $I3$ with that of a standard sample of Ag ^{129}I. In Fig. 4 we depict the temperature dependence of the relative intensity of absorption of $I3$ and AgI. As can be seen, their temperature dependences are significantly different. The slope of the AgI curve is larger than that of $I3$ and the Debye temperature (Θ_D) derived for AgI; namely, $\Theta_D=82\pm2$ K, is considerably lower than that of any other iodide as measured by ME in iodine. Thus we relate the presence of the single line to a fast quadrupole relaxation phenomenon.

In ionic crystals fluctuating electric field gradients are caused primarily by fast diffusion, or hopping, of the neighboring ions. In order to observe a fast relaxation, the hopping frequency ν_h should be larger than the quadrupole Larmor precession frequency ν_Q. In superionic crystals ν_h is of the order 10^{12} s^{-1},[2] whereas in our case ν_Q is of the order of 10^8 s^{-1} (see Table I). We now proceed to estimate the fraction of I^- that is surrounded by hopping Ag^+ cations. In a thin absorber the area of the absorption peak A_i can be written as

$$A_i=\text{const} f_i n_i \ , \tag{2}$$

where f_i is the recoil-free fraction and n_i is the concentration of iodides at site i. As in all ionic crystals the Debye-Waller factor is governed mainly by long-wavelength acoustic modes, and will be assumed to be identical for all iodide sites. Let us denote by n and N the numbers of iodides surrounded by diffusing and fixed Ag^+, respectively. Since

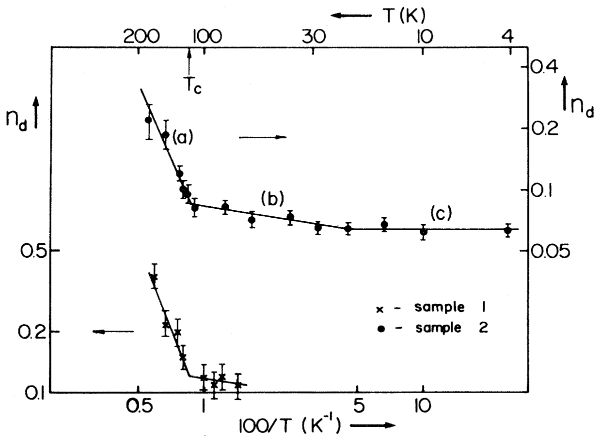

FIG. 5. Variation in temperature of n_d, the relative intensity of $I3$, assumed to reflect the concentration of local-diffusing Ag^+.

$A(I3)$ and $A(I1+I2)$ are proportional to n and N, respectively, we obtain

$$n_d = A(I3)/[A(I1)+A(I2)+A(I3)]\ , \tag{3}$$

where n_d is the fraction of iodides surrounded by diffusing Ag^+. In Fig. 5, we depict the T^{-1} variation of n_d. As can be seen, for $T < T_c$, n_d is almost constant, whereas for $T \geq T_c$ it grows exponentially, reaching values of $\sim 30\%$ at 170 K. In this experiment this is the only observation that is related to the onset of the superionic β phase, namely, with a jump in ionic conductivity. Being sensitive on an atomic scale, the ME cannot characterize long-range hopping ions. Therefore, we associate n_d with the concentration of local *diffusing* Ag. The presence of local diffusion in the process of ionic conductivity was suggested following results of quasielastic neutron scattering in AgI by Eckald *et al.*[12] From the experimental results it was concluded that the Ag diffusion can be characterized by a combination of local and long-range translational motion. Probably what the single ME line may be indicating is the process of local hopping where the cations essentially perform a three-dimensional liquidlike diffusion. Evidently, coupled with the increase in n_d at the β phase, the long-range diffusivity increases drastically, causing the sudden onset of ionic conductivity and the creation of a superionic phase. As can be seen in Fig. 5 the values of n_d are slightly different for both samples, which suggests their dependence on the history of the sample preparation.

The existence of local diffusion at temperatures as low as 4.2 K is rather unusual. A possible explanation could be based on the well-known quantum phenomenon of tunneling or the "two-level systems" proposed by Anderson *et al.*[13] and by Phillips.[14] This model was successful in explaining thermal and acoustic phenomena of glasses at low temperatures.

An interesting observation is concerned with the isomer shift (IS) of $I3$. As stated before, the IS, which is a measure of the s-electrons density at the nucleus, is quite similar to that of AgI (see Table I). Of all the iodine sites it is the most negative, suggesting a large effective volume around $I3$, consequently a large Ag-I distance. This conclusion is in agreement with the conjecture of "local diffusion" of Ag^+.

D. Dynamics of the iodide skeleton

As stated before, the areas under the absorption lines are proportional to the recoil-free fraction f of the iodides. In the harmonic approximation the f values in a Debye model can be expressed as

$$f = \exp\left\{-1.5\frac{E_R}{k_B\Theta_D(T)} \times \left[1-4\left[\frac{T}{\Theta_D(T)}\right]^2 \int_0^{\Theta_D(T)/T} \frac{x}{e^x-1}dx\right]\right\}\ , \tag{4}$$

where E_R is the nuclear recoil energy, k_B the Boltzmann constant, and $\Theta_D(T)$ is a temperature-dependent effective Debye temperature. In a pure harmonic approximation Θ_D will be independent of T.

The experimental points corresponding to the areas under the absorption lines of $I1+I2$ and of $I3$ are shown in the upper and lower parts of Fig. 3. For the case of $I1+I2$, where the temperature dependence of N [see expression (2)] is minimal, an attempt was made to fit the curve with a constant Θ_D using expression (4). The best value obtained was 100 K (see Fig. 3), which is clearly unsatisfactory at high temperatures. The best results were obtained with an empirical relation for $\Theta_D(T)$, namely

$$\Theta_D(T) = 105 - 0.075T$$

in units of K. The solid curve shows the theoretical fitting combining both f and population variation with T. The slight anharmonicity of the phonon spectra as expressed by $\Theta_D(T)$ is not surprising considering the strong variation in temperature of the Ag^+ sites as reflected in the temperature dependence of the efg. In similarity to the case of the temperature dependence of the efg, there is no discontinuity in the values or slope of $f(T)$ at $T = T_c$.

IV. CONCLUSIONS

The presence of a nonsplit single line in the absorption spectrum of $RbAg_4{}^{129}I_5$ suggests the existence of iodide sites surrounded by local-diffusing Ag^+ at all temperatures. The concentration of these iodide sites increases significantly at $T \geq T_c$ (122 K). It is reasonable to assume that the "local-diffusing" Ag concentration is correlated with the concentration of the "long-range diffusing" Ag^+ responsible for the conductivity. According to the theories of Huberman[3] and Rice *et al.*,[4] the concentration of these long-range diffusing cations shows an abrupt jump at $T = T_c$, whereas our finding for $n_d(T)$ at $T \geq T_c$ shows an activationlike increase. The ionic conductivity σ is proportional to $n(T)D(T)$, where $D(T)$ is the diffusivity. Unfortunately there is no way to measure $n(T)$ and $D(T)$ independently. If indeed the concentration of the long-range diffusion cations $[n(T)]$ also has an activationlike dependence at $T \geq T_c$, then one must search for a model where

$D(T)$ changes rapidly at $T = T_c$.

The present experiment failed to detect any onset of soft phonons at $T = T_c$. In such a case one should have observed a jump in f at $T = T_c$. The absence of soft phonons is consistent with the interpretation of Raman data in $RbAg_4I_5$.[15] There is no indication whatsoever of crystallographic rearrangements at T_c. This is concluded from the smooth variation in the temperature dependence of the efg and the isomer-shift values. Finally, from the temperature dependence of the recoil-free fraction an effective Debye temperature of 105 K at $T = 0$ is derived. A linear temperature dependence of Θ_D is assumed to account for the slight anharmonicity of the lattice dynamics at high temperatures.

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