[14] J. Avron and J. Zak, Phys. Rev. B 9, 658 (1974).

[15] H. Bross and H. Weilacher, Z. Phys. 255, 325 (1972).

[16] A. Rabinovitch, Phys. Rev. B 4, 1017 (1971).

[17] B. Simon, Ann. Math. 97, 247 (1973).

[18] R. Peierls, in *Proceedings of the Ninth International Conference on Physics of Electrons Atomic Collisions, Seattle, Washington, 1975*, edited by J. S. Risley and R. Geballe (Univ. of Washington Press, Seattle, 1975).

[19] A. Grossman, J. Math. Phys. (N.Y.) 5, 1025 (1964).

[20] F. W. J. Olver, J. Res. Nat. Bur. Stand., Sect. B 63, 131 (1959).

[21] C. Zener, in *Mathematical Physics in One Dimension*, edited by Elliot Lieb and Daniel C. Mattis (Academic, New York, 1966).

[22] R. Peierls, private communication.

NMR Relaxation in the Superionic Conductor β-LiAlSiO$_4$†

D. M. Follstaedt and Peter M. Richards
Sandia Laboratories, Albuquerque, New Mexico 87115

(Received 14 June 1976)

NMR T_1's are reported for ^{7}Li and ^{27}Al in β-LiAlSiO$_4$ which show a frequency-independent minimum as a function of temperature. The anomalous frequency independence is interpreted in terms of highly correlated one-dimensional Li$^+$ motion together with an order-disorder transition believed to occur above 500°C.

Ionic motion in superionic conductors is a phenomenon[1] of much intrinsic interest as well as having important technological implications for solid-state batteries. These compounds are characterized by a large, temperature-independent number of vacancies which provide paths of high ionic mobility. The crystal structure is often such that the paths are restricted in dimensionality, as for the one-dimensional (1D) conductor β-LiAlSiO$_4$ (LiAlSiO$_4$ with the β-eucryptite structure) studied here. These features can cause significant differences in the character of ionic diffusion from that encountered in the more widely studied cases of a small number of vacancies in a 3D lattice. In the Letter we present data on the NMR spin-lattice relaxation times T_1 of ^{27}Al and ^{7}Li in β-LiAlSiO$_4$ which show striking departures from the usual behavior expected for diffusion, and interpret them in terms of highly correlated 1D motion together with an order-disorder transition believed to occur in the compound.

The crystal structure[2] of β-LiAlSiO$_4$ is such that the Al^{3+}, Si^{4+}, and O^{2-} ions form a hexagonal lattice (similar to that of β-quartz) with channels parallel to the c axis in which the Li$^+$ ions reside. There are twice as many Li$^+$ sites as there are ions present which should permit the Li$^+$ ions to diffuse along the channels. High conductivity has been observed in glass ceramics and single crystals of these materials,[3] although the degree of anisotropy in the single crystal is as yet unknown.

At room temperature, x-ray studies[2] show that the Li$^+$ ions order, occupying alternating sites either in the planes of the Al^{3+} ions or in the Si^{4+} planes. Above 400°C the ordering is strongly reduced, disappearing somewhere above 460°C with a proposed order-disorder transition.

T_1's of the fixed-lattice ^{27}Al nucleus and of the diffusing ^{7}Li nucleus from polycrystalline ceramic samples are shown in Fig. 1 as a function of inverse absolute temperature. The 20-MHz ^{7}Li T_1's are taken from the data of Weaver and Bie-

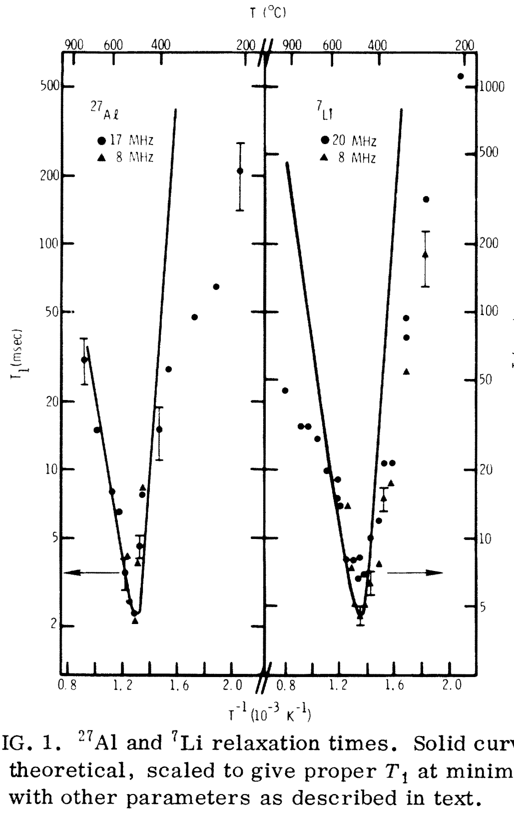

FIG. 1. ^{27}Al and ^{7}Li relaxation times. Solid curves are theoretical, scaled to give proper T_1 at minimum, and with other parameters as described in text.

feld.[4] Sample preparation has been previously presented.[3,4]

The predicted temperature and frequency dependence of relaxation caused by a fluctuating local field from a diffusing source may be seen from the classic formula derived by Bloembergen, Purcell, and Pound[5] (BPP):

$$T_1^{-1} = H_P^2 \tau_c / (1 + \omega^2 \tau_c^2), \qquad (1)$$

where ω is the nuclear Larmor frequency, and the correlation time τ_c is the average time between fluctuations of the local field H_P and is identified with the average jump time in diffusing systems. For systems with a thermally activated jump rate, (1) predicts a minimum in T_1 at $\omega\tau_c \approx 1$, with $T_1^{\min} \propto \omega$. On the low-temperature side ($\omega^2 \tau_c^2 \gg 1$) of the minimum, T_1 is frequency dependent: $T_1 \propto \omega^2 \tau_c$. Above the minimum, $T_1 \propto \tau_c^{-1}$, independent of ω.

The data show thermal activation with an energy of about 0.79 eV, in reasonable agreement with conductivity data, thus suggesting that relaxation is governed by fluctuating local fields (most likely quadrupole in origin) associated with the mobile Li^+ ions. The striking difference with Eq. (1) is the near frequency independence between 8 and 17 MHz (^{27}Al) or 20 MHz (^7Li). Additional ^7Li data at 5 MHz around the minimum show no significant difference from 8 MHz. This rules out the BPP explanation given by Weaver and Biefeld.[4] We also note that the ^7Li data have a minimum at (470 ± 15)°C which is at a lower temperature than the (510 ± 15)°C ^{27}Al minimum.

We present below a theory which explains the frequency-independent diffusion minimum for T_1 and a temperature of $(T_1)_{\min}$ which differs for the Al and Li resonances. The model is based on the 1D nature of Li^+ motion in β-$LiAlSiO_4$, which is highly restricted and correlated because there are only two sites per ion, and on the fact that the substance undergoes an order-disorder transition of the Li atoms at a temperature T_c in the vicinity of 500°C.

Below T_c there are two alternating nonequivalent Li sites labeled A and B with the A sites being dominantly occupied and therefore having the deeper potential wells. We assume that relaxation of a ^{27}Al nucleus is governed by the fluctuating electric field gradient set up by a nearest-neighbor Li^+ ion. Standard theories[6] then show that the relaxation rate is related to the Fourier transform of $P_A(t)$, the probability that a Li^+ ion is on the site A at time t given that it was there at $t = 0$.

The basic premise is that the high concentration of both particles and vacancies allows for rapid back-and-forth motion within a repeat unit (A site and B site) but no long-range migration within the time scale of interest. Specifically, the short-time motion of an ion initially in well A is restricted to its two nearest-neighbor B sites, as illustrated in Fig. 2, so that $P_A(t)$ is computed by simple transition probabilities for single-particle motion confined to at most three wells.

If we further assume that $W_{BA} \gg \omega$, where W_{BA} is the transition probability per unit time of going from a shallow B well to a deep A well, then we find that[7]

$$1/T_1 \propto W_{AB}/W_{BA}^2 \propto \exp[-(\Delta_A - 2\Delta_B)/k_B T], \qquad (2)$$

where Δ_A and Δ_B are depths of the A and B wells, respectively, and we have taken the usual dependences $W_{AB} \propto \exp(-\Delta_A/k_B T)$ and $W_{BA} \propto \exp(-\Delta_B/k_B T)$ for thermally activated hopping (W_{AB} is the $A \rightarrow B$ transition rate). It has also been assumed in Eq. (2) that the difference between the short-time approximation for $P_A(t)$, which leads to the above result, and the complete expression is a function $g(t)$ which decays so slowly that its contribution to the Fourier transform of $P_A(t)$ is negligible.

Equation (2) is a major result of the theory. It shows that if $\Delta_A > 2\Delta_B$, T_1 will increase exponentially with decreasing temperature *and be frequency independent*, whereas the BPP theories require T_1 to be proportional to ω^2 in a region where $T_1 \propto \exp(E/k_B T)$ for some activation energy E. The equation does not, however, predict a minimum in T_1 unless Δ_A and Δ_B change with temperature. But this is precisely what happens in β-$LiAlSiO_4$. X-ray data[2] show that at high temperature there is no site preference for the Li^+

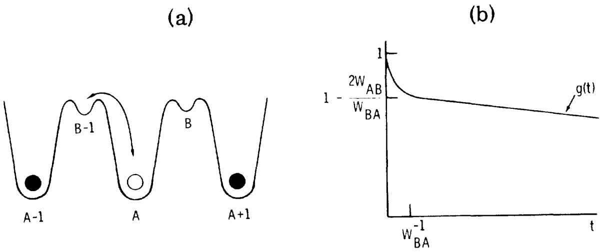

FIG. 2. (a) Schematic of assumed hopping. Ions at $A \pm 1$ are held fixed so that one initially at A can only hop back and forth. (Case shown is for $T < T_c$, where B sites are mostly unoccupied.) (b) Resulting $P_A(t)$ has rapid initial decay at rate W_{BA} to value $1 - 2W_{AB}/W_{BA}$ ($W_{BA} \gg W_{AB}$) followed by slow decay $g(t)$ after $A \pm 1$ eventually become unoccupied.

ion, which implies that $\Delta_A=\Delta_B=\Delta$ above a characteristic temperature $T_c\sim 500°\mathrm{C}$. For $T>T_c$, $W_{AB}=W_{BA}\propto\exp(-\Delta/k_BT)$, and Eq. (2) yields $1/T_1\propto\exp(\Delta/k_BT)$ under the same assumptions that $W_{AB}\gg\omega\gg 1/\tau_0$, where τ_0 is the decay time of the long-time part $g(t)$ which has been ignored. The relaxation time therefore goes through a minimum somewhere in the vicinity of T_c. There are additional terms in Eq. (2) near the minimum since the implied temperature dependence is valid only for $W_{AB}\ll W_{BA}$ or $W_{AB}=W_{BA}$. The solid curve in Fig. 1 is a plot of the complete expression with $\Delta_A=\Delta\{1+\frac{2}{3}[1-(T/T_c)^2]\}$ and $\Delta_B=\Delta\{1-\frac{2}{3}[1-(T/T_c)^2]\}$ for $T\leqslant T_c$ and $\Delta_A=\Delta_B=\Delta$ for $T>T_c$ and taking $\Delta=0.79$ eV, $T_c=528°\mathrm{C}$. The fit is insensitive to the manner in which $\Delta_B\to\Delta_A$ as $T\to T_c$ from below. For example, the choice $\Delta_A=\Delta$ and $\Delta_B=\Delta(T/T_c)^2$ works equally well.

Consider now relaxation of a ^{7}Li nucleus. It experiences a fluctuating electric field gradient from two sources. First the coupling to the rigid lattice $V_Q^{(1)}$ will be different at A sites from that at B sites. Within the approximation that an ion is confined to move no more than a nearest-neighbor distance, this produces a relaxation rate identical in form to that calculated above for the ^{27}Al nucleus. The second source comes from interaction with other Li$^+$ ions which is assumed to be proportional to the number of nearest neighbors seen by a diffusing ion. In a mean-field approximation this interaction $V_Q^{(2)}$ produces a contribution proportional to $\langle x_A\rangle-\langle x_B\rangle$, where $x_A=1$ ($x_B=1$) if site A (B) is occupied by another ion and zero otherwise, and the triangular brackets denote an ensemble average. Thus the second contribution which is related to the fluctuation of $V_Q^{(2)}$ occurs only for $T<T_c$.

One can show that for a powder average there is no interference between the contributions of $V_Q^{(1)}$ and $V_Q^{(2)}$ to $1/T_1$ so that

$$(1/T_1)_{\mathrm{Li}}\propto(1/T_1)_{\mathrm{Al}}[1+\lambda(\langle x_A\rangle-\langle x_B\rangle)^2], \tag{3}$$

where $(1/T_1)_{\mathrm{Al}}$ is the Al rate calculated from Eq. (2) and λ expresses the square of the ratio of the $V_Q^{(2)}$ to $V_Q^{(1)}$ coupling strengths. The net effect of the additional contribution to the ^{7}Li rate, as seen on the ^{7}Li curve in Fig. 1 which uses the same parameters as for the ^{27}Al T_1 curve plus $\lambda=4$, is to shift the T_1 minimum to a lower temperature without changing the measured activation energy on either side of the minimum. For $\lambda\gtrsim 4$ the shift of the minimum is 30°C, independent of λ, in close accord with the observed 40°C.

The theory outlined above is seen to produce good agreement with the main features of the relaxation data. Its major assumptions are a rapid initial decay of $P_A(t)$ which governs T_1^{-1}, and a decay time τ_0 of $g(t)$, the long-time part of $P_A(t)$, which is sufficiently slow not to affect T_1^{-1}. We are presently carrying out Monte Carlo calculations to investigate $g(t)$ and other details of the dynamics. Preliminary results support the above assumptions. If $g(t)$ is not completely negligible and/or W_{BA}^2 is not an order of magnitude greater than ω^2, there may be some residual frequency dependence which makes T_1 increase slightly with increasing frequency. These may explain the weak dependence observed in the ^{7}Li data.

The above interpretation assumes that the dominant source of relaxation is fluctuations associated with the Li$^+$-ion motion, rather than ones associated with phonons. Coupling to a soft phonon mode of frequency $\omega_p\gg\omega$ could give a frequency-independent T_1 which would then have a minimum at the order-disorder temperature T_c where ω_p goes soft. In the absence of any neutron or other data which could establish the existence or nonexistence of a soft mode in β-LiAlSiO$_4$, it is perhaps difficult to rule out this mechanism with complete certainty. However, the following evidence seems to point strongly in favor of our view of ionic motion as the controlling factor. (i) The activation energy of T_1 agrees with that of the conductivity. There is no reason to expect such agreement for phonon relaxation. (ii) The ^{7}Li and ^{27}Al relaxation rates are in a ratio consistent, to within a factor of 4, with that expected for quadrupole coupling between point-charge Li$^+$ and Al^{3+} ions. (iii) Room-temperature measurements of the ^{27}Al quadrupole splitting reveal that it is dominated by coupling to the Li$^+$ ions, so it is reasonable to assume that the fluctuating component also is governed by the Li$^+$ ions.

In conclusion, we have shown that NMR relaxation in the superionic conductor β-LiAlSiO$_4$ displays unusual characteristics which can be explained in terms of the highly correlated ionic motion brought about by the 1D channels and equal numbers of particles and vacancies together with the order-disorder transition. Similar frequency dependences have been reported[8,9] for the superionic conductors Li$_2$Ti$_3$O$_7$ and Na-β-alumina. These systems are much more susceptible to a proposed defect explanation[9] than β-LiAlSiO$_4$. But certain aspects of our model may also be important for other channeled compounds like Li$_2$Ti$_3$O$_7$.

R. M. Biefeld is gratefully acknowledged for preparing the samples. H. T. Weaver kindly allowed us to use his data. They and B. Morosin also provided helpful discussions.

---

†Work supported by the U. S. Energy Research and Development Administration under Contract No. AT-(29-1)-789.

[1] *Physics of Electrolytes*, edited by J. Hladik (Academic, New York, 1972), Vols. 1 and 2; *Fast Ion Transport in Solids: Solid State Batteries and Devices*, edited by W. van Gool (North-Holland, Amsterdam, 1973).

[2] H. Schultz and V. Tscherry, Acta Crystallogr. 28B, 2168 (1972); V. Tscherry, H. Schultz, and F. Laves, Z. Kristallogr. 135, 161 (1972).

[3] R. T. Johnson, B. Morosin, M. L. Knotek, and R. M. Biefeld, J. Electrochem. Soc. 123, 680 (1976), and private communication by these authors on single-crystal conductivity measurements.

[4] H. T. Weaver and R. M. Biefeld, Solid State Commun. 18, 39 (1976).

[5] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[6] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, Oxford, England, 1961).

[7] R. Blinc, in *Advances in Magnetic Resonance*, edited by J. S. Waugh (Academic, New York, 1968), Vol. 3, p. 166, treated NMR relaxation for a particle strictly confined to two inequivalent wells.

[8] J. B. Boyce and J. C. Mikkelsen, Bull. Am. Phys. Soc. 21, 285 (1976).

[9] R. E. Walstedt, R. Dupree, and J. P. Remeika, Bull. Am. Phys. Soc. 21, 284 (1976).

Low-Temperature Limit of the Temperature-Dependent Part of the Resistivity of Potassium

H. van Kempen, J. S. Lass,* J. H. J. M. Ribot, and P. Wyder
Physics Laboratory and Research Institute for Materials, University of Nijmegen,
Toernooiveld, Nijmegen, The Netherlands

(Received 11 August 1976)

The electrical resistivity of potassium has been measured with high accuracy between 4.2 and 1.1 K. At temperatures above 2 K the dominant term is of the form $Te^{-\theta/T}$, with $\theta = 19.9 \pm 0.2$ K, which is due to electron-phonon scattering under phonon-drag conditions. At temperatures below 2 K a weak dependence of the form AT^s is dominant, where s is between 1 and 2. Tentatively one could ascribe this term to electron-electron scattering.

The theoretical understanding of transport properties in simple metals is presently in such a state that it is possible to make very detailed predictions of the low-temperature behavior. Unfortunately, because of the lack of high-precision measurements, calculations of the low-temperature electrical resistivity have not been submitted to a detailed experimental test. It is the purpose of this Letter to present such measurements on the simple metal potassium with a hitherto unobtained precision.

Recently it has been shown theoretically that in alkali metals the simple T^5 Bloch relation should be invalid because of the presence of a phonon-drag effect.[1-3] The contribution of the electron-phonon scattering $\rho_{\text{el-ph}}$ should decrease exponentially in the low-temperature phonon-drag limit if only umklapp processes can remove momentum from the electron system. The data of Gugan[4] and Ekin and Maxfield[5] are found to be consistent with an exponential behavior between 2 and 4 K. However, these data do not allow an unambiguous determination of the all-important parameter characterizing the umklapp processes, as a result, in part, of uncertainties in the extrapolation to $T = 0$ K. In addition, as has been realized long ago,[6] there should be another contribution to the electrical resistivity, $\rho_{\text{el-el}}$, due to electron-electron interaction which should be proportional to T^2. However, there is considerable uncertainty about the exact value of the coefficient of proportionality A.[7-9] Lawrence and Wilkins[7] predict that for potassium, $A = 0.17$ pΩ cm K^{-2}. Using this value as a guide one expects that below a temperature somewhere between 1 and 2 K, $\rho_{\text{el-el}}$ should become the dominant term in the temperature-dependent part of the resistivity $\rho(T)$ and should clearly be detectable by high-precision measurements.

In this Letter we present data which not only confirm unequivocally the presence of phonon drag in potassium but also allow the electron-phonon scattering under conditions of strong phonon-drag to be specified much more exactly. We also report the observation for the first time of a low-temperature resistivity effect which could be due