ue of Γ is not known[17] and, of course, Γ itself will vary over the wide range $T \leq 100°K$ in which C_{66} is renormalized.[6]

As we have shown, the critical dynamics of dense pseudospin systems interacting via long-range forces that are dynamic in nature shows very distinct features when compared to those which have nonretarded interactions. In particular, the evolution of an initially nonconserved variable towards hydrodynamic behavior gives rise to the appearance of a Z branch in the central-peak dispersion, together with the existence of an unrenormalized relaxation rate that persists throughout the critical temperature range. Although in realistic solids short-range interactions may also be present, the signature of the interactions that we have discussed is likely to persist and be observable by light-scattering techniques.

We wish to thank Professor Roger Elliot for pointing out to us the relevance of our study to Jahn-Teller systems and to $TmVO_4$ in particular. We have also profitted from useful discussions with Professor Shang-keng Ma and Professor Lu Sham.

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Magnetic "Tagging" of Superionic Conductors

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Introducing magnetic ions (e.g., Mn^{2+}) into a superionic conductor produces large temperature-dependent effects on the NMR linewidths. This makes possible the determination of the mobile species, hopping times of 10^{-3}–10^{-12} seconds, and the range of ionic motion In magnetically "tagged" PbF_2, comparison is made between experiment and theory for the various regions of temperature in which the hopping rate of the F^- ions is slow, comparable to, or fast, compared with the F^{19} transferred hyperfine interaction with the Mn^{2+} electronic spin.

With the increasing interest in superionic conductors,[1] more attention is being given to the microscopic character of ionic motion in the solid electrolytes. NMR has been a useful tool in this regard,[2] since the resonance linewidth, $\Delta\omega \equiv T_2^{-1}$, and spin-lattice relaxation rate T_1^{-1} are sensitive to the ion hopping rate τ_c^{-1}. Motional narrowing is observed when τ_c^{-1} becomes comparable with the nuclear dipolar broadening $(\Delta\omega)_d$ and a maximum in T_1^{-1} occurs when $\tau_c^{-1} = \omega_0$, the Zeeman frequency.

We demonstrate below that a variety of supplementary information (mobile ion, hopping rate, and range of motion) may be obtained in NMR

studies by substituting some *paramagnetic* cations for the nonmagnetic ones in an ionic material. We refer to this as magnetic "tagging." An example involves the study of the F^{19} NMR in PbF_2 in which some of the Pb^{2+} ions have been replaced by Mn^{2+}.

The technique relies on the existence of both large, transferrred hyperfine interactions and a physical inequivalence of the local cation environment of a given anion in a random paramagnet.[3] At high concentrations and no ionic motion, discrete resonances are observed whose positions, widths, and intensities are a function of the number of magnetic nearest neighbors (nn) to the ion whose NMR is under investigation, as well as the field H_0, temperature T, and the magnetic ion concentration c. Rapid motion between inequivalent sites in these materials causes the discrete resonances to first broaden and then collapse into one line when the diffusion is fast enough for all ions to sample all the possible environments in a time T_2.[4] At lower concentrations, typically $c \leq 0.1$, the shifted resonances are generally not observable. However, the magnetic tagging effects are seen on the unshifted resonance at concentrations as low as one part per million.

Dramatic effects on the NMR are seen in the superionic conductor PbF_2 "tagged" with *small* amounts of Mn^{2+}. The F^{19} and Pb^{207} NMR linewidths, $(\Delta\omega)^{19}$ and $(\Delta\omega)^{207}$, vs T in single-crystal *pure* PbF_2 and PbF_2:1% Mn (nominal concentration) are shown in Fig. 1 for $T < 475$ K. With no Mn present, both $(\Delta\omega)^{19}$ and $(\Delta\omega)^{207}$ begin to exhibit motional narrowing above 325 K because of ion diffusion. The Pb^{207} results, which have not been reported before, demonstrate that motional narrowing by itself does not indicate which of the two ions (Pb^{2+} or F^-) is diffusing. However, the fact that $(\Delta\omega)^{19}$ and *not* $(\Delta\omega)^{207}$ begins to increase with T above 420 K in the Mn "tagged" PbF_2 unequivocally shows the F^- ions to be the mobile species. As to why $(\Delta\omega)^{19}$ varies as it does in the "tagged" samples we now examine in detail, for several Mn concentrations, over most of the solid-state region.

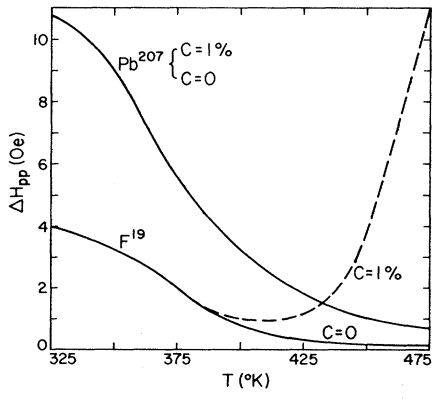

FIG. 1. Pb^{207} and F^{19} NMR linewidths vs T in pure PbF_2 and PbF_2: 1% Mn. The F^{19} resonance exhibits broadening in the doped sample at the higher temperatures while the Pb resonance does not, indicating the F^{19} ions are mobile and the motion is long ranged.

The logarithm of the derivative peak-to-peak linewidth F^{19} $(\Delta H)_{pp}$ vs T up to 1000 K is shown in Fig. 2 for PbF_2 with 0.03, 0.1, and 1% Mn. The linewidth behavior for all concentrations is characteristically different in the three temperature regions designated as (I), (II), and (III). In region (I), ($T \leq 400$ K), only the motionally narrowed linewidth of pure PbF_2 is seen, regardless of c. As τ_c^{-1} increases with further increase of T, the times between which an F^- will encounter a Mn as a nn will decrease on the average. Because of the large transferred hyperfine field ($B_{hf} = A^{19}S/\gamma\hbar \approx 15$ kOe), a Mn nn encounter will cause the precessional phase to be drastically altered. The linewidth will be determined then by the maximum time between encounters and, when this is shorter than T_2(motionally narrowed), broadening will result. One would expect, for small values of c, that

$$(\Delta\omega)^{19} \approx zc/\tau_s, \tag{1}$$

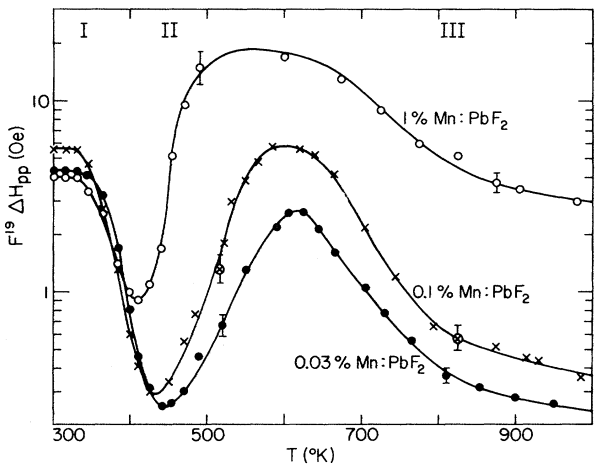

FIG. 2. Logarithm of the derivative peak-to-peak linewidths vs T of F^{19} NMR in PbF_2 doped with 0.03 and 1% Mn at 90 MHz. The three designated regions are those for which (I), ΔH_{pp} is motionally narrowed, (II), the influence of the Mn ions causes the line to be broadened and (III), the motion is fast enough to narrow the hyperfine-interaction broadening from the Mn^{2+} electronic spin.

where z (=4) is the Mn coordination number for a given F and τ_s is the time between hops into *new* sites. As the number of hops becomes large a computer simulation shows $\tau_s \rightarrow \tau_c/0.77$ in the PbF_2 structure. This region of temperature (II), $400 \leq T \leq 600$ K, has τ_c satisfying the relation $(\gamma B_{hf})^{-1} \leq \tau_c \leq zcT_2$(motionally narrowed) $\approx 10^{-5}$–10^{-7} sec.

At much higher T, all possible environments will be sampled many times in a period equal to $(\Delta\omega)^{-1}$ and a F^- will reside as a Mn nn for a time that becomes increasingly short compared with $(\gamma B_{hf})^{-1}$. In fact, if $\tau_c \ll (\gamma B_{hf})^{-1}$ the spectral density of the fluctuating hyperfine field at $\omega = 0$ and ω_0 will be appreciably reduced from its full value B_{hf} and the linewidth would be given by its "liquid-like" limit

$$\Delta\omega \simeq zc\tfrac{1}{3}(A^{19}/\hbar 2)^2 S(S+1)\tau_c. \quad (2)$$

The three regions of temperature and the values of τ_c to which they correspond are shown in Fig. 3, where the derivative peak-to-peak linewidth data are plotted as logarithm $(\Delta H)_{pp}$ vs $1/T$ for the 0.03 and 1%-Mn-doped PbF_2 samples. The predicted behavior for region (II), $(\Delta\omega)_{pp} = (0.77/\sqrt{3})zc/\tau_c$, is shown by the solid lines in Fig. 3, where we have used the conductivity-determined values[2] of τ_c vs T in pure PbF_2. The agreement between experiment and theory is seen to be quite good in region (II).

The prediction of Eq. (2) for the high-temperature region (III) are shown by the solid lines with $(\Delta\omega)_{pp} = 8.1 \times 10^{12} c\tau_c$, where τ_c vs T was obtained as above. While the observed linewidth does decrease with decreasing τ_c as expected, the agreement between experiment and theory becomes less satisfactory with increasing T. At the highest temperatures $(\Delta\omega)_{pp}^{expt} \simeq 10(\Delta\omega)_{pp}^{theor}$.

The explanation of this discrepancy is to be found in the association of the spectral density of the fluctuations of B_{hf} at relatively low frequencies ($\omega = 0, \omega_0$) with the jump correlation time τ_c determined from the conductivity data. While this is an excellent approximation at lower temperature where the vacancy number is small and their motion largely uncorrelated, it is no longer a proper description in the highly correlated superionic limit. At the higher temperatures, Raman-scattering[5,6] studies show that increasingly large low-frequency components to the ion motion appear in PbF_2, in analogy with what is seen in a strongly correlated ionic liquid. This point has been emphasized in the interpretation of the NMR data on pure PbF_2 by Boyce, Mikkelsen, and O'Keefe.[2]

The three regions as designated in Fig. 3 have their bounds set to some extent by the Mn concentration. We have marked effects even for $c = 3 \times 10^{-4}$. Suppose, however, c were as small as 10^{-6}—a not unreasonable number for nominally "pure" PbF_2. Clearly the upper bound on region (I) would extend to higher T. One might ask where deviations from the Bloembergen-Pound-Purcell (BPP) behavior[4] for the nuclear dipolar contributions to T_2^{-1} (as measured in a pulsed NMR experiment) would first occur. For $c = 10^{-6}$ we calculate these deviations to occur above 520 K.[7]

The significance of this cannot be overemphasized. Deviation from motional narrowing of the purely nuclear dipolar contributions to T_2 and T_1 will occur because of *inadvertent* magnetic "tagging" at ridiculously low concentrations of magnetic impurities. Thus while deliberate "tagging"

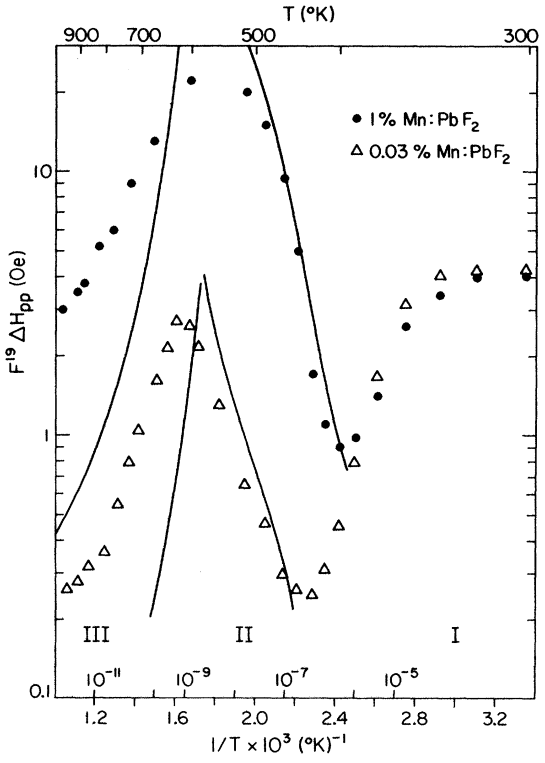

FIG. 3. Logarithm of F^{19} ΔH_{pp} vs $1/T$ for 0.03 and PbF_2: 1% Mn. The lines for region (II) are calculated from the relation $F^{19}\Delta H_{pp} = zc/(0.77\sqrt{3}\gamma\tau_c)$. In region (III) the lines represent the narrowing theory and are calculated from the relation for F^{19} that

$$\Delta H_{pp} = (0.77\sqrt{3}) - 1\frac{zc}{\gamma}\left(\frac{A^{19}}{\hbar}\right)^2 \frac{S(S+1)}{3}\tau_c.$$

is of interest itself in delineating the time domains and the long-range character of the motion in superionic conductors, it may also account for deviations from pure-crystal behavior in those cases where extraordinary precautions are not taken to remove magnetic impurities from the melt.

Measurements of T_1 and T_2 in these and related systems are now underway and will be reported elsewhere.

We would like to thank N. Nighman for the preparation of all samples used in these experiments and Dr. J. B. Boyce for discussions of his work. This work was supported in part by the U. S. Energy Research and Development Administration (E34PA-244).

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Formation and Migration Energies of Monovacancies in Tantalum

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Vacancies in thermal equilibrium were investigated by measuring the Doppler broadening of the 2γ positron-annihilation line of Ta from 35 K to the melting temperature. Experimental evidence for detrapping of positrons from vacancies at high temperatures was found. The consequences of the values obtained for monovacancy-formation and -migration enthalpies, $H_{1V}^{F} \approx 2.2$ eV, $H_{1V}^{M} \approx 1.9$ eV, for the interpretation of radiation damage and cold-work experiments are discussed.

The refractory metals are of considerable present and future scientific and technological interest, e.g., in high-temperature applications and for use in high-flux and fusion reactors. The study of point defects in these metals has been held up by difficulties related to their sensitivity to interstitial impurities (for reviews see Schaltz,[1] Nihoal,[2] and Schultz[3]). For the valid interpretation of low-temperature irradiation, cold-working, and quenching experiments reliable information on lattice vacancies is urgently required. This Letter presents the first results (on Ta) of a program designed to determine, by means of positron annihilation, the formation enthalpies H_{1V}^{F} and (by combination with self-diffusion data) the migration enthalpies H_{1V}^{M} of monovacancies in bcc refractory metals.

The material used had a residual resistivity ratio of about 5000 before the final anneal in ultra-high vacuum.[4] Sample preparation,[5,6] line-shape measurement system, line-shape deconvolution using the 497-keV γ line of ^{103}Ru, and determination of the "wing" parameter W (which is particularly sensitive to the probability that thermalized positrons annihilate with core electrons) have been described elsewhere.[7] The measurements above about 500 K were carried out in an ultra-high-vacuum system with electron-beam heating. The vacuum was about 10^{-10} Torr during measurements at low temperatures, about 10^{-9} Torr at 2700 K; and it may have been as low as 10^{-8} Torr at the highest temperatures employed. Temperatures above 1200 K were measured and controlled within a few kelvins by means of an automatic pyrometer (calibrated with a standard thermocouple), whereas at low temperatures a thermocouple was used.

Remarkable features of the temperature variation of W, which was reversible throughout, are the following (see Fig. 1): (a) Within experimental error, W is temperature independent up to about 250 K. (b) At about 250 K an S-shaped decrease of W sets in, leading to a plateau extending from about 1000 to about 1800 K. (c) The high-temperature decrease of W, which begins at about 1800 K, does not lead to saturation be-