$D_{\rm ion}$ is allowed to change by ± 10%, two Lorentzians with one of them having $D_2 = D_0$ cannot fit the experimental data. Another test of the data can be made by considering $Mg^{2+}$. A mean proton diffusion coefficient ($\bar{D} = c_1 D_1 + c_{\rm sec} D_{\rm sec} + c_0 D_0$) is available from NMR measurements[7] which were made in the fast-exchange limit. We have derived the individual $D$'s in our analysis and knowing $c_1$, $c_{\rm sec}$, and $c_0$ from the structural work we are able to predict the NMR value for $\bar{D}$. The agreement is, within error, exact. For example, at $3m$, our predicted value is $(0.76 \pm 0.05) \times 10^{-9}$ m$^2$ sec$^{-1}$ and the measured value is $(0.81 \pm 0.05) \times 10^{-9}$ m$^2$ sec$^{-1}$. At $2m$ the values are $(1.10 \pm 0.05) \times 10^{-9}$ m$^2$ sec$^{-1}$ and $(1.17 \pm 0.05) \times 10^{-9}$ m$^2$ sec$^{-1}$, respectively.

We believe this work to be the first unambiguous structural and dynamical evidence for the Frank-Wen model of solutions and it opens up the possibility of a microscopic interpretation of solution properties; it is particularly significant to note that $D_{\rm sec} \rightarrow D_{\rm ion}$ as we approach infinite dilution. Up to the present, the evidence for the original model was based almost entirely on macroscopic measurements like viscosity, thermal diffusivity, and partial molar volumes.

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# Thermalization of a Phonon Spectrum Observed by Frequency Crossing

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Measurements of the size of holes burned in the frequency spectrum of a heat current in $Al_2O_3$ by resonant phonon scattering show that the holes decay when they leave the region containing the scattering centers in distances which indicate that the crystal surface scattering is largely inelastic at 200 GHz and 2 K. The hole is monitored by observation of the scattering produced by a second ionic species tuned to the same frequency.

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When a heat current passes through an insulating solid doped with scattering centers, the centers burn holes in the frequency spectrum of the phonon current at their resonant scattering frequencies. If now the current enters an undoped region these holes should start to decay and the spectrum should approach the equilibrium spectrum for the pure crystal. A hole at frequency $\nu_i$ should decay in a distance $\sim l_I(\nu_i)$, the inelastic scattering length, to its remanent value determined by the trace impurity concentration in the undoped region.

Experiments to examine this have been made using an $Al_2O_3$ bicrystal: a crystal doped with V in one half and Fe in the other. A heat current passing from the V half, say, to the Fe half has holes burned in its spectrum at three frequencies which can be varied with a magnetic field. The holes are due to transitions within the split $^3A_2$ ground state of $V^{3+}$. The size of the holes at points in the Fe-doped end can be determined from the size of the minima in the temperature gradient, called frequency-crossing signals, which are produced when the Fe$^{2+}$ frequencies (the "detector holes") are tuned to one of the V$^{3+}$ holes (the "generator holes"). They occur because, when tuned to a hole, the Fe$^{2+}$ scattering has much less effect on the thermal conductivity, $K$. Control experiments can be made by injecting the heat current directly into the Fe-doped crystal. We note that while crossing between the transition frequencies of two different ion species has been seen previously,[1,2] the present observations are the first in which the two ions were in two different parts of the system and, as we discuss later, they indicate the possibility of much wider application of this technique.

The bicrystal, grown by the Verneuil process by Hrand Djevahirdjian SA, has a diameter of 4 mm, fine ground surfaces (20-$\mu$m features are still visible), and a total length of 40 mm, and is orientated along the crystallographic $a$ axis. It was annealed in air at 1200 °C to reduce surface damage. Thermal contacts were made with single turns of 0.3-mm-diam wire attached with epoxy resin (Stycast 2850 FT). The same heat current (~4 mW) could be injected into the crystal at either $H_{\rm V}$ or $H_{\rm FE}$ (Figs. 1 and 2). The temperature gradients (~7 mK/mm) were measured using pairs of contacts 4 mm apart each connected to 27-Ω Allen-Bradley carbon thermometers out of the main magnetic field as described elsewhere.[3] The pair nearer the interface is referred to as $T_n$, the further pair $T_f$. The field was swept through a crossing signal and the changes in the two temperature gradients were either plotted directly or stored in a signal averager (Datalab 4000). Averaging was used to improve the signal quality in some cases. The thermal conductivity of both halves of the bicrystal at 2 K was similar to that of pure $Al_2O_3$ samples of comparable dimensions and surface finish[4] as expected from previous work on crystals doped with similar amounts of Fe and V.[4] This is consistent with the narrowness of the holes in the heat current due to the Fe$^{2+}$ and V$^{3+}$ ions ($\lesssim$1 GHz).

For fields along the $c$ axis the ground states of the ions of interest, V$^{3+}$ and Fe$^{2+}$, can both be described by the spin Hamiltonian $\mathcal{H} = D(S_z^{\,2} - \frac{2}{3}) + g_{\parallel}\mu_{\rm B}BS_z$ with $S=1$ (we neglect the hyperfine splitting of V$^{3+}$) and parameters given elsewhere.[2] These ions scatter resonantly at the frequencies shown in Fig. 3, and eight frequency crossings occur below 5 T.[2] The sizes of the crossing signals $\Delta K/K$ at 2.2 K for heat flowing from the V end to the Fe ["$Q$(V → Fe)"] are shown in the top half of Table I for heat currents injected at $H_{\rm V}$ and $H_{\rm Fe}$ and some of the signals are shown in Fig. 1. From the sizes $S$ of the Fe$^{2+}$/Fe$^{2+}$ and V$^{3+}$/V$^{3+}$ signals $E$ and $F$ relative to those in analyzed samples we estimate the majority and minority concentrations (Fe in V half, V in Fe half) to be, respectively, for V$^{3+}$, 70 and <1 ppm; for Fe$^{2+}$, 2 and 0.3 ppm, which are broadly consistent with specification if we take the Fe$^{2+}$/Fe ratio to be ~1/50 as in an as-received sample in which the Fe$^{2+}$ concentration was estimated roughly by EPR.[5] These sizes did not vary detectably with the position of the contacts showing that each half of the sample was rather homogeneous. Also, as expected, they did not depend

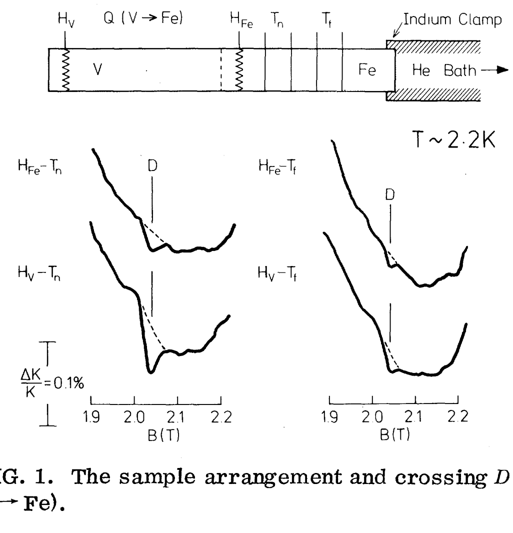

FIG. 1. The sample arrangement and crossing $D$ for $Q$(V → Fe).

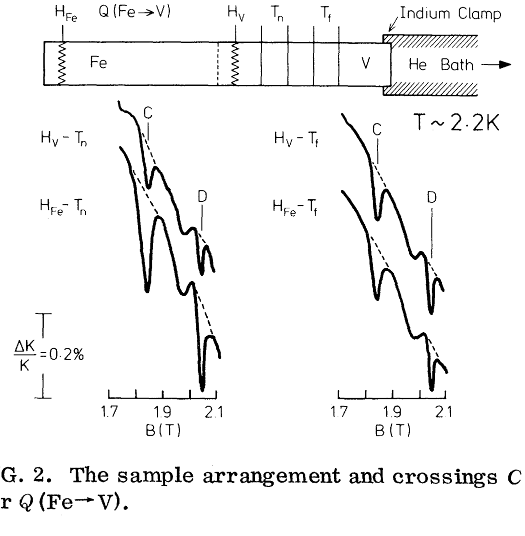

FIG. 2. The sample arrangement and crossings $C$ and $D$ for $Q$(Fe → V).

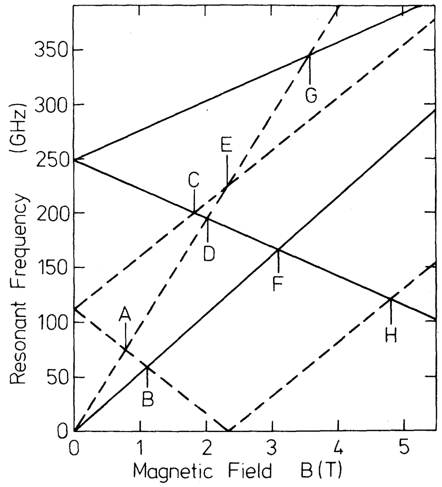

FIG. 3. Frequency crossings between V$^{3+}$ (solid lines) and Fe$^{2+}$ (dashed lines) for fields along the $c$ axis.

on the injection point of the current [for signal $F$ this refers to $Q$(Fe → V)].

It is clear, however, from Table I that at $T_n$ centered 6 mm from the interface the Fe$^{2+}$/V$^{3+}$ signals $C$, $D$, $G$, and $H$ are considerably larger for $H_V$ injection than for $H_{Fe}$ injection. This is illustrated for $D$ in Fig. 1. We conclude that the holes burned in the heat current by V$^{3+}$ ions in the V half are still substantially greater, 6 mm from the interface, than their remanent values measured by injecting heat at $H_{Fe}$. (The remanent values $S_r$ are determined by the minority concentration of V$^{3+}$.) However, at $T_f$ centered 12 mm from the interface, as seen in Table I and for $D$ in Fig. 1, the signals produced by $H_V$ injection are *not* significantly different from the remanent values ($H_{Fe}$ injection). So the holes burned in the V half decay almost completely in 12 mm.

In the bottom half of Table I and in Fig. 2, we show data for configuration "$Q$(Fe → V)" where the heat current now passes from the Fe half to the V half. Again it is very clear that 6 mm from the interface the signals obtained when the heat current is passed through the Fe sample ($H_{Fe}$ injection) are much bigger (apart from $G$) than their remanent values ($H_V$ injection) but again they have largely decayed in 12 mm. The signal size is expected to depend principally on the weaker of the two crossing processes[6] and so this decay indicates that at 6 mm from the interface, the generator hole is smaller than the detector hole except perhaps for line $G$.

Assuming that the signals decay exponentially to their remanent values, we obtain $\exp(6/l_I) = (S_6 - S_r)/(S_{12} - S_r)$. Subtraction of $S$ from the background introduces an error ~0.1$S$ with additional errors due to noise of ~0.01%; so from the table we obtain an upper limit of $l_I \sim 4$ mm at 194 GHz and 2 K. This limit gives signal sizes close to the interface of $S_0 \sim 5S_6$, comparable to those obtained in a crystal containing both V and Fe in concentrations close to their majority values here.[2] The values of $l_I$ obtained at 119 and 199 GHz and also at 1.5 K are the same to within the fairly large experimental error, suggesting that $l_I$ cannot depend very strongly on frequency and temperature. Similar results were obtained on a second bicrystal which was

TABLE I. Size of frequency crossings $\Delta K/K$ (%). Noise level ~ 0.01%. Signals visible only as a change of slope indicated by asterisks; undetected signals by ellipses. Data were not completed for lines $E$ and $H$ because of magnet damage. Crossing frequencies in gigahertz are given in brackets.

| | $A$ (75) | $C$ (199) | $D$ (194) | $E$ (224) | $F$ (166) | $G$ (347) | $H$ (119) |
|---|---|---|---|---|---|---|---|
| | | | | $Q$ (V→Fe) | | | |
| $H_{Fe}$-$T_n$ | 0.08 | 0.02 | 0.02 | 0.90 | ⋯ | * | * |
| $H_V$-$T_n$ ($S_6$) | 0.09 | 0.08 | 0.06 | 0.90 | ⋯ | 0.05 | 0.05 |
| $H_{Fe}$-$T_f$ | 0.08 | 0.02 | 0.02 | 0.90 | ⋯ | * | * |
| $H_V$-$T_f$ ($S_{12}$) | 0.10 | 0.02 | 0.02 | 0.90 | ⋯ | * | 0.02 |
| | | | | $Q$ (Fe→V) | | | |
| $H_V$-$T_n$ | ⋯ | 0.09 | 0.10 | 0.13 | 0.16 | 0.06 | 0.13 |
| $H_{Fe}$-$T_n$ ($S_6$) | ⋯ | 0.24 | 0.21 | 0.13 | 0.20 | 0.06 | 0.30 |
| $H_V$-$T_f$ | ⋯ | 0.10 | 0.10 | | 0.18 | 0.06 | |
| $H_{Fe}$-$T_f$ ($S_{12}$) | ⋯ | 0.10 | 0.10 | | 0.17 | 0.06 | |

from a different boule but comparably doped and prepared.

Since $l_I \sim 4$ mm at three discrete frequencies it seems very probable that this is its value throughout the range they span. Now if this inelastic scattering were from a bulk process, the resultant phonon mean free path from this plus boundary scattering ($l_B \sim 4$ mm) would be ~2 mm which is only half that calculated from our thermal-conductivity data. Further evidence against it being from a bulk process comes from heat-pulse measurements showing that under similar conditions the bulk mean free path in pure $Al_2O_3$ $\gtrsim 8$ cm,[7] and as we have noted the $V^{3+}$ and $Fe^{2+}$ ions can only reduce this in very narrow bandwidths. We conclude that the inelastic scattering must be from a surface process since of course at the surface this additional scattering cannot reduce $l_B$ to below 4 mm. If $\alpha$ ($\alpha \leq 1$) is the probability that a phonon colliding with the surface is inelastically scattered, we can write $l_I^{-1} = \alpha l_B^{-1}$ and so the experiments suggest $\alpha \sim 1$. This is much higher than the values of $\alpha \lesssim 0.1$ for very carefully prepared Si surfaces and $\alpha \sim 0.25$ for mechanically polished $Al_2O_3$ measured from the decay of "$2\Delta$" phonons at 280 GHz and 1 K.[8] It seems possible that the inelasticity is due to surface damage, perhaps to vibrating dislocations[9] or even to two-level systems now known to be created in crystalline material by neutron damage.[10] The fact that the present values of $\alpha$ for $Al_2O_3$ are higher than in previous work could indicate a higher degree of damage although it could also be significant that we can detect quasielastic scattering involving frequency changes down to 1 GHz, an order of magnitude smaller than in the previous work. Attempts to remove the damage by chemical polishing were abandoned because of problems arising from the very anisotropic polishing rate. The measurements have been repeated, however, after the bicrystals were annealed for 5 h in nitrogen at 1500 °C. This does not affect the surface topography but previous work has shown that it reduces the dislocation density.[11] The results are inconclusive. In one bicrystal the decay was much reduced with $l_I \sim 20$ mm but in the other there was no significant change. Further experiments are planned after annealing at 1700 °C which largely removes surface structure.

The two principal conclusions from this work are (1) that it is possible to detect when the energy separation of two levels in one part of a crystal becomes equal to that of a different ion in another part by passing a heat current between them, and (2) that phonon scattering by the surfaces of mechanically polished crystals can be very inelastic. The indications here that this inelastic scattering at $Al_2O_3$ surfaces can be reduced by surface treatment and earlier evidence for this at Si surfaces[8] shows that the frequency-crossing technique could be of much wider application if it should prove possible to obtain bonds transparent to phonons at these frequencies. This would clearly also be of value to other techniques. Previous bonds at lower frequencies using amorphous glues between mechanically polished surfaces are not transparent at the higher frequencies used here and we plan experiments with crystalline glues between surfaces annealed at 1700 °C. It might also be possible to do reflection spectroscopy off films deposited, grown, or implanted at carefully prepared surfaces.

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