

## Mechanisms for nonthermal effects on ionic mobility during microwave processing of crystalline solids

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Models for nonthermal effects on ionic motion during microwave heating of crystalline solids are considered to explain the anomalous reductions of activation energy for diffusion and the overall faster kinetics noted in microwave sintering experiments and other microwave processing studies. We propose that radiation energy couples into low (microwave) frequency elastic lattice oscillations, generating a nonthermal phonon distribution that enhances ion mobility and thus diffusion rates. Viewed in this manner, it is argued that the effect of the microwaves would not be to reduce the activation energy, but rather to make the use of a Boltzmann thermal model inappropriate for the inference of activation energy from sintering-rate or tracer-diffusion data. A highly simplified linear oscillator lattice model is used to qualitatively explore coupling from microwave photons to lattice oscillations. The linear mechanism possibilities include resonant coupling to weak-bond surface and point defect modes, and nonresonant coupling to zero-frequency displacement modes. Nonlinear mechanisms such as inverse Brillouin scattering are suggested for resonant coupling of electromagnetic and elastic traveling waves in crystalline solids. The models suggest that nonthermal effects should be more pronounced in polycrystalline (rather than single crystal) forms, and at elevated bulk temperatures.

### I. INTRODUCTION

The unique characteristics of ceramics, ceramic/refractory composites, and glasses have led to their widespread application in many areas of the consumer and industrial marketplace. Ultimately, it is hoped that these materials will address needs in such advanced applications as high-temperature engine components, structural components for space vehicles/station, shock and radiation-resistant high-voltage insulators, specialty waveguides, structural and engine components for advanced aircraft, etc. Significant improvements in materials and material properties, as well as in cost and ease of manufacture, are needed, however, before many of these applications are realized. To this end, perhaps the greatest improvements are to be found in the technique of sintering, due to the major influence that sintering has in determining critical microscopic and macroscopic properties of the final product, as well as its obvious role as a relatively inexpensive manufacturing process for brittle, refractory solids.

Sintering is conventionally accomplished in ohmically heated ovens as a conduction process. That is, heat is deposited on the outside of the object (by radiant,

conductive, and/or convective heat transfer) and diffuses inward by conduction. Therefore, to avoid excessive thermal gradients, a slow heat-up and heat-down cycle must be used. One result of this approach is that the driving force for densification of a powder compact is lost during heating to surface diffusion that, in many cases, is more rapid than grain boundary or lattice diffusion at low temperatures. Consequently, incomplete, nonuniform densification plagues the conventional process.

Hot pressing and hot isostatic pressing (HIPing) subject the crystalline lattice to large deformation stresses, thereby enhancing the driving force for exchange of an ion-vacancy pair during diffusion. This lowers sintering temperatures, reduces the heat-up time, and reduces the negative impact of surface diffusion. As a result, hot pressing or HIPing can yield near-theoretical densities and strength, small grain size, high grain uniformity, and freedom from microstructural cracks. However, preparing samples for hot pressing or HIPing is a difficult, time-consuming, and labor-intensive process. Furthermore, hot-pressing complex object shapes that are premachined in the green-body state is often difficult or impractical.

An alternative to ohmic heating is to use coherent microwave heating. To simplest order, one would expect advantages for microwave sintering over conventional oven sintering similar to the advantages of microwave food processing over conventional oven cooking: (1) microwave power can be generated and transmitted to the heated object more efficiently than by resistively heating a conventional oven element, and (2) the heating is more uniform and rapid since the radiation is absorbed directly inside the object, rather than depending on inward conduction from the surface.

As a result of these features, one might expect microwave sintering to yield some of the advantages of hot pressing (microstructural uniformity, strength, theoretical density, etc.) while permitting efficient, pressureless processing of shapes, as in conventional sintering. Some of the most remarkable results, supporting such expectations, have been recently reported by researchers at Oak Ridge National Laboratory.<sup>1,2</sup> Indeed, their observations go beyond these bulk effects, suggesting that different microscopic mechanisms for the motion of ions are responsible for the differences between microwave and conventional sintering. For example, experiments with beta-alumina suggest an apparent reduction in activation energy of 70% during microwave sintering, when compared with conventional (pressureless) sintering. Specifically, the inferred activation energy for the conventional process was 575 kJ/mole, compared to an inferred activation energy of 170 kJ/mole for the microwave process. In both processes, equal bulk temperatures were maintained based on thermocouple measurements. In similar experiments with single crystal sapphire, microwave heating was observed to yield enhanced tracer diffusion kinetics for  $^{18}\text{O}^{2-}$ . Moreover, empirically inferred activation energies for ion diffusion based on a thermal process model were 20% lower for microwave versus conventional heating. No fundamental physical mechanisms have yet been established to explain these remarkable observations. A physical explanation must concentrate on the effect of long-wavelength (i.e., low-energy) radiation on the ionic diffusion that results in the densification of a powder compact.

In sintering, the driving force for ionic motion is the decrease in surface Gibbs energy that occurs as free surface area is replaced by solid-solid interfaces (i.e., grain boundaries). The diffusion fluxes involved can be analyzed from a Fick-Einstein perspective; that is

$$j_i = -\left(C_i \tilde{D}_i / k_B T\right) \nabla \eta_i \quad (1)$$

where  $j$  is flux,  $C$  is concentration,  $\tilde{D}$  is the chemical diffusion coefficient,  $\eta$  is electrochemical potential (all of the  $i$ -th species),  $k_B$  is Boltzmann's constant, and  $T$  is the temperature of the solid. As with all phenomenological

descriptions of kinetic processes, Eq. (1) represents the product of a driving force and a species mobility: the driving force is the gradient in electrochemical potential; the mobility is contained in the chemical diffusion coefficient. Ionic mobility involves the motion of point defects, and the chemical diffusion coefficient can be described as a function of point defect concentration and point defect mobility. In a thermal process, the dependence is separable; that is, one can write:

$$\tilde{D} \propto e^{-Q/k_B T} \propto [\text{defect concentration}] \cdot [\text{defect mobility}] \quad (2)$$

for diffusion driven by a Boltzmann distribution of ionic energies. A corollary to Eq. (2) is that, for thermal diffusion, the activation energy  $Q$  can be expressed as the sum of that for formation of point defects ( $Q_{PD}$ ) and that for the mobility of defects ( $Q_M$ ):

$$Q = Q_{PD} + Q_M \quad (3)$$

The Oak Ridge observation that plotting logarithms of microwave sintering rates against bulk inverse temperatures as measured by a thermocouple yields lower slopes than for conventional sintering has been interpreted<sup>1</sup> as a decrease in activation energy. However, we argue that for parameter regimes relevant to sintering, the activation energy  $Q$  is approximately equal to the enthalpy  $H$ . However,  $H$  (and thus  $Q$ ) is largely determined by intrinsic material characteristics such as the atomic bonds and structure of the compound. This has two implications. First, it is unlikely that the microwave radiation alters the atomic bonds of the medium and therefore it is unlikely that the microwave radiation reduces  $H$  or  $Q$ . Second, in the regime where  $Q \approx H$  we expect  $Q$  to be insensitive to temperature, and by extension, insensitive to the details of the ion energy or phonon distribution. Therefore, our interpretation of the Oak Ridge observation cited above is that microwave heating decreases the sensitivity of diffusion to bulk temperature, rather than truly decreasing the activation energy itself. In other words, something else must be helping to drive the diffusion process other than the random or thermal ion motions which probably determine bulk temperature as measured by a thermocouple. However, it is probably still valid to use Eqs. (2) and (3) and argue that the mechanistic of microwave heating that increase diffusional kinetics in a crystalline solid, while decreasing the temperature sensitivity of diffusion, must involve either increasing the concentration of point defects, increasing the intrinsic mobility of point defects, or both.

It is questionable whether microwave radiation could increase the concentration of point defects. The activation enthalpy for anion or cation vacancy formation in MgO, for example, is on the order of 3 eV; in

NaCl, the value is approximately 1.2 eV (these values represent the range of vacancy formation enthalpy for small cation/large anion simple compounds). Activation enthalpy for the motion/mobility of these vacancies is smaller, approximately 40 to 60% of the formation enthalpy. Since the microwave photon energy of  $\sim 10^{-4}$  eV is so small compared to any of these activation enthalpies, it is most likely that microwave absorption will proceed in classical (continuum) fashion, having first impact on that process with the lowest activation energy, i.e., the mobility of point defects. As mobility of point defects is related to vibrations of the crystal lattice, we propose the following as a candidate hypothesis for the effect of microwave radiation on diffusion kinetics: *The microwave radiation generates a nonthermal phonon distribution in the (poly)crystalline lattice and thereby enhances the mobility of crystal lattice ions. This leads to enhanced diffusion and to enhanced sintering rates.* It is also believed that similar nonthermal effects are responsible for unusual observations reported in other microwave heating processes.<sup>3</sup> In the remainder of this paper, we present simplified models for an ionic crystal lattice immersed in a microwave field, and discuss the implications regarding the hypothesis proposed above.

**II. MODEL AND DISCUSSION**

**A. Linear coupling to elastic oscillations**

We start with a highly simplified kinetic model for oscillations in a perfect one-dimensional crystal lattice. The lattice is modeled classically as a uniformly spaced chain of point masses (representing the ions) joined by ideal springs (representing the lattice bonds).<sup>4-6</sup> The classical spring model should be valid, provided that the temperature exceeds the Debye temperature for the solid compound.<sup>4</sup> (The Debye temperatures for most of the material compounds of interest will typically be less than or equal to 300 degrees Kelvin.) In addition, each ion is coupled to a bound electron by an ideal spring. Each electron collectively represents an atomic electron cloud which can be displaced from the nucleus by an external electric field. To model the effect of the microwaves, we subject the charges (ion and electron masses) to a sinusoidal external electric field. The model system is schematically illustrated in Fig. 1. The simplified model assumes that all of the ions in the lattice chain of Fig. 1 are identical. Allowing for the multiple ion species normally present in a compound will quantitatively refine, but not qualitatively alter, the essence of our arguments.

To describe mathematically the system of Fig. 1, we assume that the spring forces are linear, central, restoring forces with spring constants

$$\kappa_i = \frac{m_i}{2} \omega_i^2 \tag{4}$$

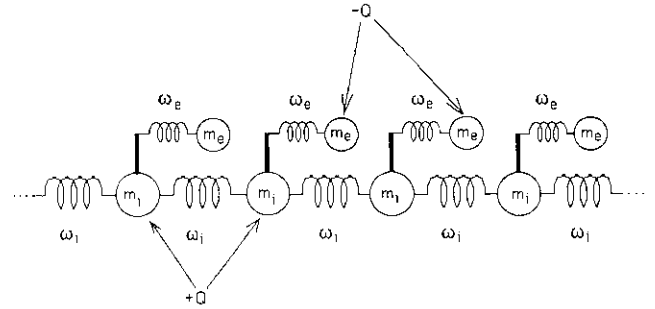


FIG. 1. Classical, one-dimensional mass-and-spring model for ions and valence electron clouds in a perfect crystal lattice.

$$\kappa_e = \frac{m_e m_i}{m_e + m_i} \omega_e^2 \approx m_e \omega_e^2 \tag{5}$$

In Eqs. (4) and (5),  $\kappa_i$  ( $\kappa_e$ ) is the spring constant for one ion-ion (ion-electron) bond, and  $m_i$  ( $m_e$ ) is the mass of a single ion (electron). As shown in Fig. 1,  $\omega_i$  is the resonant oscillation frequency for the single spring connecting two ions, while  $\omega_e$  is the resonant frequency for a single ion-electron pair.

Strictly speaking, the linear force model is valid only for small displacements  $\delta x$  of the ions (and valence electron clouds) relative to their equilibrium positions; i.e.,  $\delta x / \rho_0 \ll 1$ , where  $\rho_0$  is the equilibrium ion spacing. Consistent with this constraint, and as suggested by the illustration in Fig. 1, we consider only nearest-neighbor interactions in the chain.

For large displacements about equilibrium, the linear model will have several inaccuracies. For example, the linear model will usually predict larger fluctuation amplitudes than a localized nonlinear force model such as those of Refs. 7 and 8. Also, a linear force will not model irreversible conversion of a coherent oscillation mode to thermal fluctuations. At this stage, however, we are more interested in a qualitative assessment of oscillation energy transfer efficiency from microwave radiation to ion motion, and therefore neglect these limitations of the linear model. A significant perturbation of ion motions is a prerequisite to sustaining an observable nonthermal phonon distribution in the presence of dissipation. Accurately modeling the phonon distribution, including the irreversible thermalization of microwave phonons, would require the consideration of nonlinear effects.

We now have a system of coupled linear harmonic oscillators under the influence of an external oscillatory forcing function (the microwave electric field). Note that nonthermal, discrete frequency phonon distributions are a natural consequence in harmonically forced linear systems. Since damping effects are neglected, the system dynamics may be analyzed and understood in terms of the normal modes of oscillations of the lattice.<sup>9</sup> We suggest at least two types of normal modes that may be

effectively driven by the microwave field: (1) resonant coupling to a single pair of ions bound by a weak bond (small-scale resonant coupling), and (2) coupling to zero-frequency modes in which the centers of mass of aggregates of ions with overall electric charge are accelerated.

1. Small-scale resonant coupling

We first consider under what conditions one might expect microwave radiation to resonantly drive small-scale elastic oscillations, involving only a few ions on a localized scale (such sites could serve as localized sources for excitation of propagating phonons). This is unlikely to occur within a perfect crystal lattice, as ion-ion bonds are characterized by resonant frequencies in the range of infrared photons, while the electron-ion bonds are characterized by resonant frequencies approaching the optical regime. For example, the resonant restrahl frequency  $\omega_i$  of a single spring and two ion masses (cf. Fig. 1) is typically of the order  $\omega_i \sim 10^{12} - 10^{14} \text{ s}^{-1}$ . This is too large for direct coupling from microwave photons characterized by frequencies  $\omega_{em} \sim 10^9 - 10^{11} \text{ s}^{-1}$ . Thus, in perfect single crystal compounds, we expect slight coupling between microwave energy and locally resonant perturbations of the ions.

In polycrystalline compounds, however, the possibility for weaker surface bond modes exists at the various microscopic surface and grain boundary interfaces. This is especially true for green bodies prior to sintering. Hence, we can imagine the possibility of small scale or localized microwave phonon excitation through resonant coupling to weak surface bonds. Similarly, in both polycrystalline and single-crystal compounds, the presence of point defects (vacancies) can lead to localized resonances at frequencies much lower than the typical restrahl frequency  $\omega_i$ .<sup>10</sup>

2. Zero-frequency coupling

This normal mode is a zero-frequency mode in which the center of mass of an aggregate of ions is displaced by the microwave field. An individual ion's displacement  $x_i$  is the sum of a center-of-mass displacement  $\mathfrak{X}$  plus a displacement  $r_i$  relative to the center-of-mass:

$$x_i = \mathfrak{X} + r_i \tag{6}$$

The center-of-mass motion for  $N_i$  ions and  $N_e$  electrons is determined by the equation

$$(N_i m_i + N_e m_e) \ddot{\mathfrak{X}} = (N_i - N_e) Q E \tag{7}$$

where  $E$  is the electric field strength and  $Q$  is the net charge on the ion (or electron cloud). Equation (7) implies that there will be no coupling to this zero-frequency mode unless there exists some (local) charge imbalance

in the chain of coupled atoms—i.e.,  $N_e \neq N_i$ . A configuration in which zero-frequency mode coupling is possible is sketched in Fig. 2. Associating an effective charge of  $(N_i - N_e)Q \approx N_{\text{eff}}|e|$  with a chain of identical (i.e., regular) atoms (where  $|e| = 1.6 \times 10^{-19} \text{ C}$ ) leads to local displacements of every ion in the chain according to:

$$|\mathfrak{X}| \sim \frac{N_{\text{eff}} e E}{N_i m_i \omega^2} = \frac{f e E}{m_i \omega^2} \tag{8}$$

where  $f$  represents the fractional charge imbalance,  $f = N_{\text{eff}}/N_i$ .

Under what conditions can we expect (local) charge imbalance? Transition metal impurities can create appropriate electronic lattice defects. Free surfaces, grain boundaries, and dislocations can (because of their structural role in the creation of lattice vacancies and because of the difference in formation energy of intrinsic cation and anion vacancies) create localized excess charge in the lattice; thus, in polycrystalline compounds, the possibility exists for stimulating microwave-frequency phonons near extended lattice defects. Note that this explanation is consistent with the localized, microscopic regions of enhanced conductivity, as hypothesized by Ho.<sup>11</sup> In addition, charged anion vacancies, because of their property to act as electron donors, combined with the role of dislocations discussed above, can allow such arguments to be extended to single crystals. Nevertheless, possibilities for localized charge imbalance would appear to be greater in polycrystals than in single crystals. It has also been shown that relatively small (microwave-induced) deviations of the ion kinetics from random thermal motions are sufficient to make substantial changes to ion jump probabilities and ion mobility.<sup>12</sup> Based on the discussion in Ref. 12, a value of

$$|\mathfrak{X}|/\rho_0 \geq 0.001 - 0.01 \tag{9}$$

should be considered a significant nonthermal effect, where  $\rho_0$  is the equilibrium lattice ion spacing,  $\rho_0 \sim$

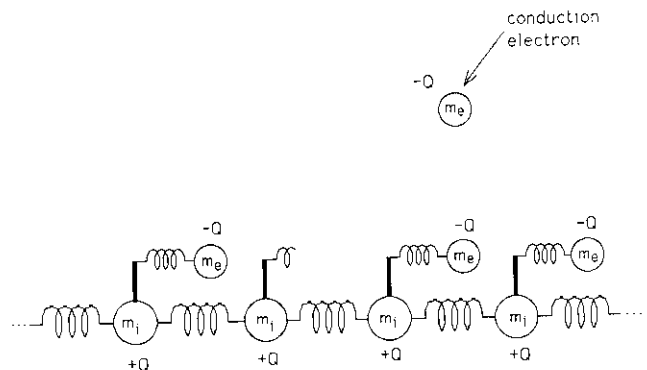


FIG. 2. Idealized classical atomistic chain model with a localized charge imbalance needed for microwaves to couple to a zero-frequency phonon mode or center-of-mass perturbation.

1 Å. Equation (9) can also be understood from the following qualitative argument. At common sintering temperatures (~1000–2000 °C), the average ion's thermal motion involves fluctuations  $\delta x$  of order  $\delta x \sim 0.1 \text{ Å}$ .<sup>8</sup> For microwave-induced perturbations satisfying Eq. (9),  $|\Re|/\delta x \sim 1\text{--}10\%$ , which is a significant deviation from thermal equilibrium.

To get order-of-magnitude estimates for the local charge imbalance concentrations needed to couple to a zero-frequency mode, we consider the experimental parameters of the Oak Ridge experiments.<sup>1,2,13,14</sup> For example, based on a measured microwave cavity  $Q$  of ~130 000, input power of ~1000 W, cavity volume of ~0.4 m<sup>3</sup>, sample dielectric constant  $\epsilon_r \sim 9.7$  (alumina), and frequency of ~28 GHz, it can be estimated that the electric field strength was of the order of  $10^5\text{--}10^6 \text{ V/m}$  during these sintering experiments. From Eqs. (8) and (9) and for a typical lattice ion spacing of  $\rho_0 \sim 1 \text{ Å}$ , significant nonthermal phonon effects from microwave heating requires local effective bound-charge concentrations of  $f \geq 0.001$ . This is consistent with the level of impurities expected in even the highest commercial grades of ceramic powders and compacts (e.g., 99.8% for alumina). Again, it is expected that this effect is more likely to exist locally near grain boundaries and microscopic surfaces (where impurities concentrate) within polycrystalline samples than within high purity single crystal samples.

### B. High temperature effects

So far, we have hypothesized that anomolous effects observed in microwave sintering experiments might be explained by nonthermal mechanisms involving either resonant coupling to low energy bond surface or point defect states, or coupling to local concentrations of charge in the lattice.

High temperatures (viz., well above room temperature, but below that normally required for effective sintering) will have several effects relevant to our hypothesis. First, as the temperature of the compound rises, the conduction electron concentration also rises according to the thermal expression:

$$\frac{n_e}{n_{\text{atom}}} = \exp[-U_b/k_B T]$$

where  $U_b$  is the bandgap energy. A threshold electron concentration (reciprocally implying a threshold local bound charge concentration)—necessary for strong coupling to zero-frequency modes—may be reached at temperatures somewhat below that normally required for conventional sintering.

The second important effect of elevated temperatures is that as thermal oscillations of ions in the lattice increase in amplitude, the springs representing their bonding to the lattice become increasingly nonlinear.

This increases the possibility of resonant harmonic and subharmonic microwave coupling to elastic oscillations, as well as to difference or beat frequencies,  $\omega_{em} \approx \Omega_j - \Omega_k$ , where  $\Omega_{j,k}$  are high frequency lattice modes that differ by only a small fraction,  $(\Omega_j - \Omega_k)/\Omega_{j,k} \ll 1$ . Such nonlinear effects are central to the photon/phonon coupling mechanism discussed in the following section.

### C. Nonlinear coupling of electromagnetic and elastic traveling waves

In the previous section, we considered mechanisms for coupling energy from the radiation's fluctuating electric field into localized (standing) ion oscillations. For such phenomena, the principal criterion is to identify circumstances which match the microwave and the phonon frequency.

In this section, we consider the feasibility of resonant coupling between electromagnetic (microwave) and elastic (phonon) traveling waves. Resonance in such wave-wave interactions requires not only frequency-matching, but also phase (or wavelength) matching. That is, we simultaneously require matching frequencies  $\omega_{em} = \Omega_a$  and phase velocities  $c_{em} = v_a$  where  $em$  indicates the electromagnetic wave and  $a$  indicates the acoustic or phonon wave. Certainly, at microwave frequencies one can find bulk phonon modes which satisfy frequency-matching. It is equally certain, however, that electromagnetic phase velocities  $c_{em} \sim 10^7\text{--}10^8 \text{ m/s}$  are several orders of magnitude greater than elastic wave phase velocities  $v_a \sim 10^3\text{--}10^5 \text{ m/s}$ . Thus direct, linear coupling between propagating microwaves and propagating elastic waves is improbable. Hence, we must consider nonlinear processes such as microwave absorption through inverse Brillouin scattering.

For example, suppose that due to finite bandwidth in the microwave source, there are (at least) two frequency components  $\omega_1$  and  $\omega_2$  of high power microwave radiation present, such that  $|\omega_1 - \omega_2| \ll \omega_1, \omega_2$  and  $\omega_1 \approx \omega_2 \approx \omega_{em}$ . We now consider the frequency- and phase-matching conditions necessary for these two electromagnetic waves to couple resonantly to an elastic wave with frequency  $\Omega_a$ :

$$\omega_1 - \omega_2 = \Omega_a, \tag{10}$$

and

$$\mathbf{k}_1 - \mathbf{k}_2 = \mathbf{K}_a, \tag{11}$$

where  $\mathbf{k}_1, \mathbf{k}_2$  are the electromagnetic wavevectors and  $\mathbf{K}_a$  is the elastic wavevector. Since  $\omega_1 \approx \omega_2 \approx \omega_{em}$ ,  $|\mathbf{k}_1| \approx |\mathbf{k}_2| \approx k_{em}$ , and hence

$$K_a = |\mathbf{K}_a| \approx 2k_{em} \sin(\theta/2) \tag{12}$$

where  $\theta$  is the scattering angle between  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . But  $K_a \approx \Omega_a/v_a$  and  $k_{em} \approx \omega_{em}/c_{em}$ , so that by

substituting into Eq. (12) we obtain

$$\frac{\Omega_a}{\omega_{em}} \approx 2 \frac{v_a}{c_{em}} \sin(\theta/2) \leq 10^{-3} \sin(\theta/2) \quad (13)$$

Note that the original assumption of  $\Omega_a \approx |\omega_1 - \omega_2| \ll \omega_1, \omega_2$  is satisfied for any choice of  $\theta$  because  $v_a \ll c_{em}$ .

We now turn to the question of whether the three-wave mixing process discussed above is relevant to the Oak Ridge experiments. First, it is expected that scattering within the overmoded cavity as well as within the ceramic sample will yield an electromagnetic  $\mathbf{k}$ -spectrum that is essentially isotropic. Thus, if a particular value of  $\theta$  is required for resonant photon-to-phonon coupling, it is probable that electromagnetic wave components will exist to satisfy the necessary scattering angle. Second, it has already been established that due to the large cavity  $Q$ , the electric field strengths within the cavity are very high. This is probably necessary for the proposed nonlinear absorption process. Third, most high power microwave sources can be expected to produce a finite spectral bandwidth of order  $10^{-6} \leq \Delta\omega/\omega \leq 10^{-2}$ . Such a bandwidth would include spectral frequency components  $\omega_1$  and  $\omega_2$  which satisfy Eq. (13). Hence, it appears feasible that resonant (and thus nonthermal) transfer of microwave energy to crystal lattice phonons can occur between two high intensity electromagnetic waves (in the microwave regime) to a low frequency (radio frequency or lower) elastic wave under the conditions present during the Oak Ridge experiments. The remaining question, the strength of the coupling, requires an analysis that is beyond the scope of this qualitative discussion. As mentioned earlier, however, it is expected that the strength of such nonlinear coupling will increase at elevated temperatures.

For illustrative purposes, we will consider one more mechanism for nonlinear three-wave mixing during microwave sintering of ceramics. For this case, we consider the resonant coupling between two high frequency elastic waves and one lower frequency electromagnetic wave. The frequency- and phase-matching conditions for this process are:

$$\Omega_1 - \Omega_2 = \omega_{em}, \quad (14)$$

and

$$\mathbf{K}_1 - \mathbf{K}_2 = \mathbf{k}_{em}. \quad (15)$$

To simplify the algebra, we will arbitrarily restrict discussion to the more limited case where  $\Omega_1 \approx \Omega_2 \approx \Omega_a$ , so that  $|\mathbf{K}_1| \approx |\mathbf{K}_2| \approx K_a$ . Following steps similar to the previous case, we obtain the resonance condition

$$\frac{\omega_{em}}{\Omega_a} \approx 2 \frac{c_{em}}{v_a} \sin(\theta/2) \sim (10^3 \text{ to } 10^5) \sin(\theta/2) \quad (16)$$

Note that  $\Omega_1 \approx \Omega_2 \approx \Omega_a$  can only be satisfied consistent with Eq. (13) when the microwave frequency is much

less than the elastic wave frequency  $\omega_{em} \ll \Omega_a$ . But this is consistent only with the resonance condition Eq. (16) for  $\theta \approx 0$ , due to the large difference between the electromagnetic and elastic wave phase velocities (here  $\theta$  is the angle between  $\mathbf{K}_1$  and  $\mathbf{K}_2$ ). Nevertheless, for  $\theta \approx 0$  the analysis suggests that resonant energy transfer from high intensity microwave radiation to higher frequency elastic waves is possible by nonlinear three-wave mixing. Again, a calculation of the coupling strength remains to be considered. Elevated temperatures will also enhance the coupling strength of this process by increasing the nonlinearity of the material's ionic susceptibility.

### III. SUMMARY

We have proposed that observations of anomalous reductions in apparent activation energy for microwave versus conventional sintering are due to nonthermal phonon distributions excited by the microwave field. Thus, the effects of the microwaves would not be to reduce the activation energy, but rather to render the use of a "Boltzmann-like" thermal model inappropriate for the inference of activation energy. Significant excitation of nonthermal phonons by the microwave field appears to be possible through one or more of the following mechanisms: (1) localized resonant coupling to weak bond surface modes or point defect modes, (2) zero-frequency mode coupling requiring localized concentrations of charge imbalance, and (3) three-wave mixing involving either two closely-spaced microwave frequencies and a one low frequency elastic wave, or two high frequency elastic waves and one microwave frequency electromagnetic wave. Mechanisms (1) and (2) can be described as linear coupling processes and mechanism (3) is a nonlinear effect, i.e., inverse Brillouin scattering. Mechanisms (1) and (2) favor polycrystalline over single crystal forms, at least at lower temperatures, and this is consistent with reported experimental observations.<sup>1,2</sup> Higher temperatures would enhance the probabilities for mechanisms (2) and (3) in both single- and polycrystal compounds. Finally, it is suggested that similar non-thermal effects may explain other anomalous observations during microwave processing.<sup>3</sup>

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