

- 1926), p. 1.  
<sup>2</sup>D. E. Schuele and C. S. Smith, *J. Phys. Chem. Solids* **25**, 801 (1964).  
<sup>3</sup>F. W. Sheard, *Phil. Mag.* **3**, 1381 (1958).  
<sup>4</sup>R. A. Bartels and D. E. Schuele, *J. Phys. Chem. Solids* **26**, 537 (1965).  
<sup>5</sup>M. Arenstein, R. D. Hatcher, and J. Neuberger, *Phys. Rev.* **132**, 73 (1963).  
<sup>6</sup>E. R. Cowley and R. A. Cowley, *Proc. Roy. Soc. (London)* **A287**, 259 (1965).  
<sup>7</sup>R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, *Phys. Rev.* **131**, 1030 (1963).  
<sup>8</sup>G. Peckham, *Proc. Phys. Soc. (London)* **90**, 657 (1967).  
<sup>9</sup>F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).  
<sup>10</sup>G. R. Barsch and B. N. N. Achar, *Phys. Status Solidi* **35**, 881 (1969).  
<sup>11</sup>R. W. Roberts and C. S. Smith, *J. Phys. Chem. Solids* **31**, 619 (1970).  
<sup>12</sup>R. W. Roberts and C. S. Smith, *J. Phys. Chem. Solids* (to be published).  
<sup>13</sup>R. A. Miller and C. S. Smith, *J. Phys. Chem. Solids* **25**, 1279 (1964).  
<sup>14</sup>S. S. Mitra, *Phys. Status Solidi* **9**, 519 (1965).  
<sup>15</sup>M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, 1954).  
<sup>16</sup>T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, *Proc. Roy. Soc. (London)* **A279**, 62 (1964).  
<sup>17</sup>S. S. Mitra, C. Postmus, and J. R. Ferraro, *Phys. Rev. Letters* **18**, 455 (1967).  
<sup>18</sup>J. R. Ferraro, C. Postmus, S. S. Mitra, and C. J. Hoskins, *Appl. Opt.* **9**, 5 (1970).  
<sup>19</sup>A. C. Holt and M. Ross, *Phys. Rev.* **1**, 2700 (1970).  
<sup>20</sup>C. Feldman, J. L. Feldman, G. K. Horton, and M. L. Klein, *Proc. Phys. Soc. (London)* **90**, 1182 (1967).  
<sup>21</sup>D. H. Saunderson, *Phys. Rev. Letters* **17**, 530 (1966).

PHYSICAL REVIEW B

VOLUME 3, NUMBER 4

15 FEBRUARY 1971

## Zero-Field Magnetic Relaxation in Cerous Magnesium Nitrate below 0.2 K<sup>†</sup>

A. C. Anderson and J. E. Robichaux

*Department of Physics and Materials Research Laboratory,  
 University of Illinois, Urbana, Illinois 61801*

(Received 8 September 1970)

The magnetic relaxation of Ce<sup>3+</sup> in cerous magnesium nitrate (CMN) has been measured in zero applied field at temperatures in the range 0.02–0.2 K. For pure CMN, the relaxation is phonon bottlenecked, with some evidence for resonant trapping. Addition of Pr impurity to CMN reduces the severity of the bottleneck, apparently by excitation of the Pr<sup>3+</sup> hyperfine levels via a two-phonon process. With sufficient Pr content, the relaxation becomes dominated by the thermal boundary resistance between the bath and the crystal lattice.

### I. INTRODUCTION

The processes of energy transfer between the spin system of cerous magnesium nitrate (CMN) and the environment of the crystal, or "bath," have been studied extensively by a number of experimental techniques. Many of the data below ~1 K are indicative of the occurrence of a bottleneck in the energy transfer. That is, the net transfer of energy is much slower or less efficient than the direct spin-phonon relaxation process whereby a spin flip creates a phonon in a crystal lattice which always remains in thermal equilibrium with its environment. In order to study the bottlenecked processes, we have observed the magnetic relaxation of CMN in zero applied field over a temperature range of 0.02–0.2 K.

The transfer of energy under the condition of a bottleneck can be understood in the following manner. The difference in population of the levels of the lowest Kramers doublet is

$$\delta N = N \tanh(h\nu/2kT_s),$$

where  $N$  is the total number of Ce<sup>3+</sup> ions,  $h\nu$  is the separation in energy of the two levels, and  $T_s$  is the temperature<sup>1</sup> of the spin system. The rate that energy is transferred from the spin system is then

$$\dot{Q} = -kNT_s [(h\nu/2kT_s) \operatorname{sech}(h\nu/2kT_s)]^2,$$

where it is assumed that the sample is at a uniform spin temperature. Defining a resistance to thermal transfer by  $\mathcal{R} \equiv (T_s - T)/\dot{Q}$ , where  $T$  is the temperature of the environment of the crystal, one obtains

$$dT_s/(T_s - T) \simeq -(dt/kN\mathcal{R}) [(h\nu/2kT) \operatorname{sech}(h\nu/2kT)]^{-2} \\ \equiv dt/\tau.$$

Here we have assumed that the observed relaxation time constant  $\tau$  is much greater than the time constant for direct spin-phonon relaxation  $\tau_d$ , and that the spins are close to thermal equilibrium with the environment,  $(T_s - T)/T \ll 1$ . Without the latter assumption, the equations are nonlinear.<sup>2</sup> Both assumptions are valid under the experimental conditions used in the present work. Hence,

$$\tau = kN\mathcal{R}[(h\nu/2kT)\operatorname{sech}(h\nu/2kT)]^2 = \mathcal{R}C_s, \quad (1)$$

where  $C_s$  is the heat capacity of the spin system.

A variety of bottlenecked processes have been discussed in the literature,<sup>2-11</sup> the spatially limited phonon bottleneck being the most prevalent.<sup>3, 4, 12, 13</sup> In this case, a band of phonons of energy  $h\nu$  and width  $\Delta\nu$  find themselves in closer thermal contact with the spin system at temperature  $T_s$  than the rest of the lattice modes at temperature  $T$ . Assuming the relaxation-time approximation to be valid for phonons, we have  $dn/dt = -n/\tau_{ph}$ , where  $n$  is the number of phonons of energy  $h\nu$  and  $\tau_{ph}$  is an appropriate relaxation time for inelastic phonon processes. Thus, the transfer of energy  $\dot{Q}$  from this band of phonons to the lattice is

$$\dot{Q} = (12\pi V\nu^3 h\Delta\nu/\tau_{ph}v^3) [(e^{h\nu/kT} - 1)^{-1} - (e^{h\nu/kT_s} - 1)^{-1}],$$

where  $V$  is the volume of the sample and  $v$  the phonon velocity. If, again,  $(T_s - T)/T \ll 1$ , then

$$\dot{Q} = (T_s - T)(3\pi V\nu^4 h^2 \Delta\nu/\tau_{ph}v^3 kT^2) \operatorname{csch}^2(h\nu/2kT),$$

so that the thermal resistance may be written

$$\mathcal{R} = (\tau_{ph}v^3 kT^2/3\pi V\nu^4 h^2 \Delta\nu) \sinh^2(h\nu/2kT). \quad (2)$$

Combining Eqs. (1) and (2), we obtain

$$\tau = (N/V)(\tau_{ph}v^3/12\pi\nu^2 \Delta\nu) \tanh^2(h\nu/2kT). \quad (3)$$

In the limit that  $h\nu \ll kT$ ,

$$\mathcal{R} \simeq \tau_{ph}v^3/12\pi\nu^2 \Delta\nu kV \quad (4)$$

and

$$\tau \simeq (N/V)(\tau_{ph}v^3 h^2/48\pi k^2 \Delta\nu) T^{-2}. \quad (5)$$

If the line shape of the band of phonons is other than rectangular as assumed here, a numerical constant of order unity appears in the above expressions, and  $\Delta\nu$  becomes the half-width of the line.

The parameter  $\tau_{ph}$  represents the mean time required for a phonon to undergo an inelastic collision, or  $\tau_{ph} = \lambda/v$ , where  $\lambda$  is the mean free path for such collisions. Frequently it is assumed that  $\lambda \sim L$ ,  $L$  being the smallest dimension of the sample. That is, the phonon encounters some dissipative process at the wall. In practice, values of  $\lambda$  both larger<sup>14, 15</sup> and smaller<sup>16, 17</sup> than  $L$  have been deduced from various types of measurements on various crystals, as well as  $\lambda \sim L$ .<sup>12, 18</sup> Hence, inelastic collisions may also occur within a crystal.

We now turn our attention explicitly to CMN (sometimes diluted with La). Ruby *et al.*<sup>13</sup> measured  $\tau$  by an EPR method and found the temperature dependence to be consistent with a phonon bottleneck, Eq. (3). Mess<sup>19</sup> reports on direct measurements of  $\mathcal{R}$  and demonstrates the proper temperature and magnetic field dependence for a phonon bottleneck, Eq. (2). Mess, however, did not find a dependence on sample size. Brya and Wagner,<sup>20</sup> on the other hand, observed the expected

temperature dependence and a dependence on size (as well as surface condition). A possible explanation of this inconsistency in size dependence is that the small dimension of the sample was parallel to the crystalline  $c$  axis for Mess, and perpendicular to the  $c$  axis for Brya and Wagner. It has been observed that the mean free path (for all collisions) can be much greater in a direction perpendicular to the  $c$  axis.<sup>21</sup> A long mean free path perpendicular to the  $c$  axis has also been demonstrated in the resonant-phonon coupling of spatially separated populations of Pr and Ce in lanthanum magnesium nitrate.<sup>22</sup>

The demonstration of a phonon avalanche<sup>23</sup> and of Brillouin scattering from the hot band of phonons  $\Delta\nu$ <sup>24</sup> give final proof of the presence of a phonon bottleneck in CMN, although these experiments do not further elucidate the nature of the bottleneck itself.

Most of the data referred to above were obtained in fields of  $\sim 1000$ – $4000$  G. Below  $\sim 0.5$  K, relaxation by either the Orbach or the Raman process is negligible in CMN.<sup>13</sup> As the field is reduced,  $\tau$  [Eq. (5)] remains essentially constant while  $\tau_d \sim H^{-4} \sim \nu^{-4}$ .<sup>25</sup> Hence, at low fields one might expect  $\tau_d$  to become greater than  $\tau$ ; in other words, that the relaxation would no longer be bottlenecked. However, Mess<sup>19</sup> reports data down to 100 G which are still compatible with a phonon bottleneck, and furthermore it can be deduced from his data that  $\mathcal{R} \sim \nu^{-2} \sim H^{-2}$  down to zero external field (internal field  $\sim 50$  G). It therefore appears that  $\tau_d$  in CMN remains relatively short and, indeed, the dominant spin-phonon relaxation mechanism in zero applied field and at temperatures down to  $\sim 0.02$  K.<sup>26</sup>

The present work was undertaken to further investigate the magnetic relaxation of CMN at zero field and low temperature ( $0.02 < T < 0.2$  K). Our interest was further enhanced by the fact that, although no systematic study was ever made, the thermal relaxation time of our CMN magnetic thermometers<sup>27</sup> was always observed to be faster (by  $\sim 10^2$ ) than the bottlenecked rate expressed by Eq. (5). We present in Sec. III evidence that essentially three bottlenecked processes are operative in CMN, the dominant mechanism being determined by the concentration of Pr impurity and by the temperature range. We first present in Sec. II a brief description of the experimental approach.

## II. EXPERIMENTAL TECHNIQUE

The CMN crystals were grown on Teflon flats by desiccating a saturated aqueous solution at a temperature of  $0^\circ\text{C}$ , and were doubly recrystallized. The starting materials were of the highest available purity.<sup>28</sup> The crystals were transparent and optically perfect, although this does not guarantee crystalline perfection.<sup>21</sup> Samples of 1 cm width

and 2.5 cm length were cut from the flat hexagonal crystals using a wet-string saw. The thickness dimensions were always parallel to the crystalline  $c$  axis, and were intentionally varied between 0.1 and 0.4 cm.

The samples were suspended between the prongs of an Epoxy yoke. A bundle of straight loose 0.005-cm-diam insulated Cu wires permeated with Apiezon N grease was pressed against the surfaces of the sample, one bundle on either side. These wires were connected thermally to a dilution refrigerator. This technique eliminated the cleavage of a thin layer from the surface of the crystal with thermal cycling. The coil of a mutual-inductance bridge<sup>27</sup> was placed over the sample in order to observe transient behavior of the spin temperature. The axis of this coil was oriented perpendicular to the crystalline  $c$  axis. The field from a Helmholtz pair was oriented mutually perpendicular to both the mutual-inductance coil and the crystalline  $c$  axis. The field of the Helmholtz pair (2–10 G) was left on (off) until thermal equilibrium was established between the CMN spin system and the dilution refrigerator. The field was then quickly turned off (on) and the transient behavior recorded. Most relaxations were recorded directly on an  $x$ - $y$  recorder, although a multichannel signal averager was sometimes used for the fastest relaxations encountered. The noise level was lower with zero applied field and so transients were normally recorded only as the field was turned off, since the relaxation appeared to be independent of whether the field had been turned on or off. The relaxations were exponential, with the exception of those obtained from crystals of the highest purity, as will be discussed in Sec. III. The temperatures during equilibrium were determined with a calibrated resistance thermometer, since the CMN samples had large and uncertain shape corrections<sup>29</sup> which made them unsuitable for magnetic thermometry.

In order to analyze the relaxation data, one must have some knowledge of the thermal-contact resistance, or boundary resistance,<sup>30</sup> which exists at the interface between the CMN samples and the bundle of wires. This thermal resistance was measured by isolating one bundle of wires and placing an electrical heater and calibrated resistance thermometer on this bundle. In this situation one measures the sum of two boundary resistances plus the bulk thermal resistance of the CMN sample in a direction parallel to the crystalline  $c$  axis. The bulk resistance of the sample was expected to make a negligible contribution to the net thermal resistance.<sup>21</sup> This was proven by using as a sample a CMN crystal containing  $\approx 0.5\%$  Pr impurity. This impurity produces a depression in the thermal conductance of the crystal near 0.07 K.<sup>21</sup> Since there was no depression in the measured net thermal

conductance, effectively only the boundary resistance was being measured. The magnitude of the boundary resistance was a factor of 2–3 larger than that deduced from similar measurements on chrome potassium alum<sup>31</sup> and for a CMN-brass contact.<sup>19</sup> All three measurements used Apiezon N grease as a thermal-contact agent, although this in itself has a minor influence on the boundary resistance.<sup>32</sup>

The heat capacity of CMN must also be known in order to obtain a value for the thermal resistance  $\mathcal{R}$  [Eq. (1)]. Although the  $\text{Ce}^{3+}$  ions in CMN are highly dilute, there is nevertheless a magnetic dipolar interaction so that the derivation of  $C_s$  leading to Eq. (1) is not strictly valid. That is, the temperature dependence of  $C_s$  is not exactly  $T^{-2}$ . We therefore use the measured  $C_s$  for highly pure CMN as given by Mess *et al.*<sup>33</sup> and by Hudson and Kaeiser.<sup>34</sup> For the purposes of the present work, these two measurements of the spin heat capacity are in agreement.

### III. RESULTS AND DISCUSSION

A calculation of  $\tau$  for our samples using the phonon-bottleneck process of Eq. (3) and  $\tau_{ph} \approx L/v$  is represented as line A in Fig. 1 assuming  $\Delta\nu \approx 100$  G,  $v \approx 2 \times 10^5$  cm/sec,  $N/V = 1.6 \times 10^{21}$  cm<sup>-3</sup>, and  $L = 0.2$  cm. Also, the relaxation time for these samples determined by  $\tau_B = R_B C_s$ , where  $C_s$  and  $R_B$  are the measured heat capacity and thermal boundary resistance, is shown by line B.  $\tau_B$  represents the limiting relaxation time for any sample, and is to be included in the general classification of bottlenecked processes. If the time constant were to result from thermal diffusion, the relaxation time becomes  $\tau_D = L^2 C_s / 4\pi K_{11}$ , where  $K_{11}$  is the thermal conductivity measured parallel to the  $c$  axis.<sup>21</sup> The behavior in this limit would be roughly as shown by curve C in Fig. 1. The fact that this relaxation time is a factor of  $10^2$  smaller than that due to the boundary resistance means that a common temperature exists throughout the lattice for our samples.

A measured relaxation time for a typical "off-the-shelf" sample is shown by D in Fig. 1. The relaxation time is seen to be about a factor of  $10^2$  faster than the expected bottleneck of curve A, as was mentioned in Sec. I. We guessed that the bottleneck in these samples was being relieved by impurities, since the samples had been grown from starting materials of only nominal purity. In addition, we simultaneously were making thermal-conductivity measurements on the same group of crystals during which we observed the resonant scattering of phonons. The resonant scattering was correctly ascribed to the Pr impurity,<sup>21</sup> which suggested that  $\tau$  might also be dominated by this ion. This idea seemed reasonable in view of the fact that  $\text{Pr}^{3+}$  is a non-Kramers ion and therefore interacts strongly with the lattice.

"Pure" crystals of CMN ( $\text{Pr}/\text{Ce} \sim 5 \times 10^{-6}$ ) were grown and  $\tau$  measured, with the result represented by curve E of Fig. 1. These results were reproducible from sample to sample, and were independent of the sample thickness. Also shown ( $\times$ ) are the computed values of  $\tau = \mathcal{R}C_s$ , using values of  $\mathcal{R}$  calculated from the data given by Mess for zero field.<sup>19</sup> The agreement is surprisingly good. From  $\tau \sim T^{-2}$ , as observed in the present work, and  $\mathcal{R} \sim H^{-2}$ , as observed by Mess, the relaxation is apparently bottlenecked by the process of Eq. (3), with  $\tau_{\text{ph}}$  being limited by the inelastic scattering of phonons within the crystal. Using Eq. (3), one estimates  $\tau_{\text{ph}} \approx 10^{-7}$  sec and  $\lambda \approx 0.02$  cm. This short

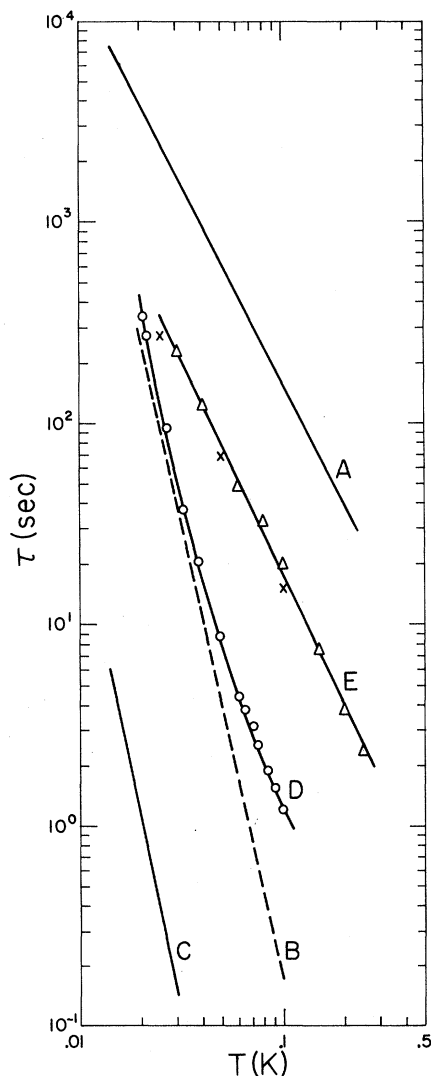


FIG. 1. Time constant  $\tau$  for thermal relaxation of  $\text{Ce}^{3+}$  ions in CMN vs temperature.  $\Delta$ : high-purity CMN;  $\circ$ : CMN of nominal purity;  $\times$ : values for high-purity CMN calculated from Ref. 19. The other curves are explained in the text.

mean free path is consistent with the fact that  $\tau$  was found not to be a function of sample dimensions either in the present work or in that of Mess.

However, the short phonon mean free path of  $\lambda \approx 0.02$  cm is not consistent with the much longer mean free paths obtained in measurements of the thermal conductivity (where the phonons had ten times higher frequency,<sup>21</sup> i. e.,  $T \lesssim 0.02$  K) or magnetic resonance (where the CMN was diluted with La<sup>20,22</sup> by  $\text{Ce}/\text{La} \approx 4 \times 10^{-3}$ ). The inconsistency can be removed if two assumptions are made concerning those phonons which lie within the band of width  $\Delta\nu$  which is resonant with the  $\text{Ce}^{3+}$ : (i) The phonons are scattered by planes of imperfections lying with their normals parallel to the  $c$  axis (evidence for the presence of such planes has been presented in Ref. 21) and (ii) the phonons undergo effectively elastic scattering due to resonant absorption and subsequent reemission by the  $\text{Ce}^{3+}$  ions. Thus, the phonons diffuse to the lattice imperfections in a time  $\tau_{\text{ph}} \sim 10^{-7}$  sec, and, once reaching a plane of imperfections, undergo sufficient encounters with that plane to undergo an inelastic process. For planes separated by a distance  $2x \approx 0.005$  cm,<sup>21</sup> one obtains from  $x = (\frac{2}{3} v \Lambda \tau_{\text{ph}})^{1/2}$  a step length or mean free path for elastic scattering of  $\Lambda \approx 5 \times 10^{-4}$  cm. Thus, the imprisonment of resonant phonons is rather marginal [and Eq. (3) remains valid] for our concentrated CMN, and would be absent in the diluted samples of Refs. 20 and 22. There is further evidence for diffusive transport of the resonant phonons in that the relaxation was slightly nonexponential for the high-purity crystals. Hence, the spin temperature, though uniform on a gross scale, was somewhat nonuniform on a scale of  $\sim 10^{-3}$  cm.

Having established that the Pr impurity was responsible for "breaking" the bottleneck, we next attempted to understand in what manner the Pr entered into the relaxation of the  $\text{Ce}^{3+}$  states. Samples were intentionally doped with known amounts of Pr in the ratios  $\text{Pr}/\text{Ce} = 1.5 \times 10^{-5}$ ,  $1.8 \times 10^{-3}$ , and  $8 \times 10^{-3}$ . The temperature dependencies shown in Fig. 2 were obtained. It should first be noted that these results reproduced to  $\sim \pm 5\%$  if the samples were remounted and rerun. The results reproduced to  $\sim \pm 20\%$  or better for samples cut from different crystals having the same nominal concentration of Pr.

Two facts are readily evident in Fig. 2: (a)  $\tau$  decreases with increasing concentration of Pr, and (b)  $\tau$  becomes increasingly sensitive to the sample thickness as the Pr concentration is increased. Removing the thermal-contact wires from one face of the crystal produced results identical to doubling the thickness of the sample. Thus, the thickness effect is associated with the thermal boundary resistance and not a size-dependent phonon relaxation time. It is also noted from Fig. 2 that for samples

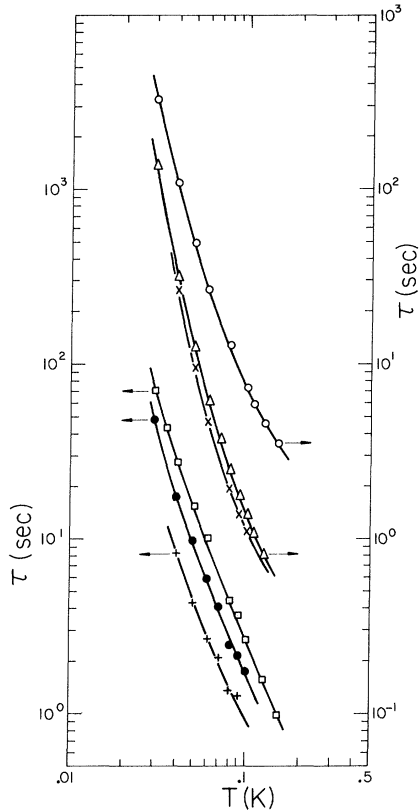


FIG. 2. Time constant  $\tau$  for thermal relaxation of  $\text{Ce}^{3+}$  in CMN crystals of various thicknesses and containing Pr impurity. O:  $\text{Pr}/\text{Ce} \approx 1.5 \times 10^{-5}$ , any thickness from 0.1 to 0.4 cm;  $\Delta$ :  $\text{Pr}/\text{Ce} \approx 1.8 \times 10^{-3}$ , 0.40 cm thick;  $\times$ :  $\text{Pr}/\text{Ce} \approx 1.8 \times 10^{-3}$ , 0.10 cm thick;  $\square$ :  $\text{Pr}/\text{Ce} \approx 8 \times 10^{-3}$ , 0.40 cm thick;  $\bullet$ :  $\text{Pr}/\text{Ce} \approx 8 \times 10^{-3}$ , 0.22 cm thick;  $+$ :  $\text{Pr}/\text{Ce} \approx 8 \times 10^{-3}$ , 0.10 cm thick. Note the two separate vertical scales.

having  $\text{Pr}/\text{Ce} = 1.5 \times 10^{-5}$  ( $1.8 \times 10^{-3}$ ), the relaxation time is independent (nearly independent) of the sample dimensions. Thus, the relaxation process at this concentration is also internal to the crystal. Finally, it is noted that  $\tau$  varies as  $T^{-4}$  or faster at low temperatures. Therefore, the relaxation is not via direct coupling between the Ce and Pr spin systems as, for example, by spin diffusion. It is concluded that the Ce relaxes to the phonon band with which it is resonant, and that Eqs. (3) and (5) are appropriate. The temperature dependence of the thermal resistance  $\mathcal{R}$ , Eq. (4), then arises from the temperature dependence of  $\tau_{\text{ph}}$ .

The behavior of the relaxation time  $\tau$  of Fig. 2 can be understood in terms of the analog of Fig. 3(i), an  $R$ - $C$  electrical circuit. Here  $\mathcal{R}$  represents the thermal resistance between the Ce and the lattice,  $C_s$  is the heat capacity of the Ce spin system,  $C_L$  is the heat capacity associated with the lattice, and  $R_B$  is the boundary resistance between sample and refrigerator. Our measured boundary resis-

tance may be used for  $R_B$  since both involve phonons of the same frequency range.

The electronic levels of the  $\text{Pr}^{3+}$  ion are split by interaction with the magnetic hyperfine field from the Pr nucleus as shown by insert (ii) of Fig. 2. Therefore, a Schottky-type heat capacity is associated with the Pr impurity, though somewhat broadened due to interaction of the ion with local strain fields.<sup>21</sup> The resulting specific heat is shown in Fig. 3 together with  $C_s$ , which is related to the  $\text{Ce}^{3+}$ . Since the coupling of the non-Kramers  $\text{Pr}^{3+}$  ion to the lattice is so strong,<sup>12</sup> its heat capacity is to be associated with the lattice. Therefore, the Pr below 0.3 K completely dominates the lattice heat capacity  $C_L$ .

The differential equations appropriate to the discharge of  $C_s$  in Fig. 3, insert (i), may be solved for the relaxation time  $\tau$ . Since  $\mathcal{R}$  is the unknown,

$$\mathcal{R} = \tau/C_s + (C_L/\tau - 1/R_B)^{-1}. \quad (6)$$

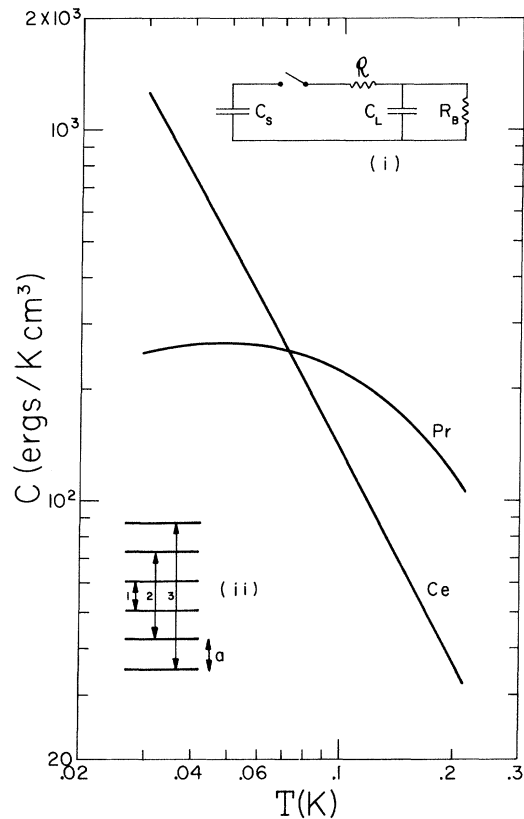


FIG. 3. Specific heat of CMN taken from Refs. 33 and 34, and of Pr in CMN (in the amount  $\text{Pr}/\text{Ce} = 1.8 \times 10^{-3}$ ) as obtained from Ref. 21. The Pr specific heat for other concentrations may be scaled from the graph. Insert (i) is an  $R$ - $C$  circuit which may be used as an analog to the thermal relaxation of CMN as explained in the text. Insert (ii) indicates the separation of electronic levels of  $\text{Pr}^{3+}$  in CMN due to hyperfine interaction ( $a \approx 0.05$  K).

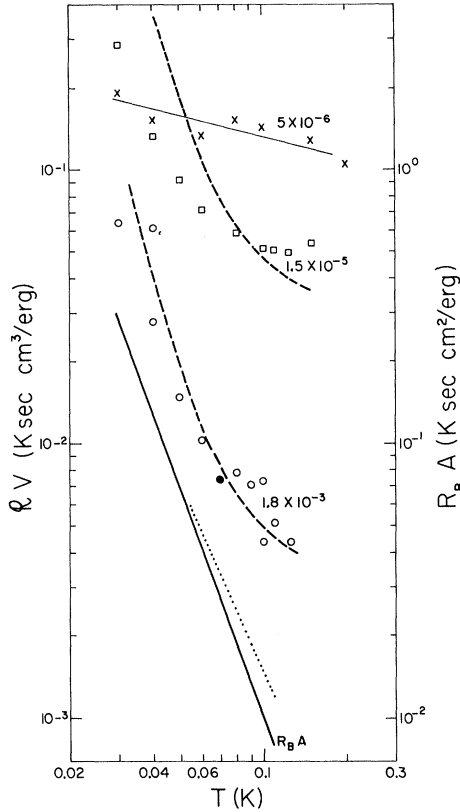


FIG. 4. Thermal resistance  $\mathcal{R}V$  (for a unit cube) to energy transport between the lattice and phonons resonant with the  $\text{Ce}^{3+}$  ions in CMN. The ratio of Pr/Ce for each set of samples is noted. Only experimental data were used in calculating these points. The dashed lines are calculated from Eq. (7) in the text. Also shown for comparison is the measured boundary resistance  $R_B A$  for a unit square. The dotted line includes the thermal resistance of the copper wires between sample and refrigerator, which was simply added to  $R_B$  for purposes of computation.

$C_L$ ,  $C_s$ ,  $\tau$ , and  $R_B$  are all known from experiment. Using the values of  $\tau$  from Fig. 2,  $C_L$  and  $C_s$  from Fig. 3, and  $R_B$  from Fig. 4, the thermal resistance for a unit volume  $\mathcal{R}V$  has been calculated and plotted in Fig. 4. The shape of the curves for the sample containing  $1.5 \times 10^{-5}$  Pr and, to a lesser extent, the 0.1-cm-thick sample with  $1.8 \times 10^{-3}$  Pr are nearly independent of the experimental parameters  $C_L$  and  $R_B$ . Results for samples containing  $8 \times 10^{-3}$  Pr are not included in Fig. 4 since in these cases  $\tau \approx C_L R_B$  in the second term of Eq. (6).<sup>35</sup> The Ce relaxation in this case is "bottlenecked" by the inefficient energy transfer at the crystal surfaces due to the acoustic mismatch. It should also be noted that the curve in Fig. 4 for the sample with Pr/Ce =  $1.5 \times 10^{-5}$  is distorted in shape, since whatever process relaxes phonons in the complete absence of a Pr impurity is, in the present case, still

acting in parallel with the Pr.

It was argued above that the values of  $\mathcal{R}V$  plotted in Fig. 4 are related to Eq. (4), and that the temperature dependence displayed in Fig. 4 results from the temperature dependence of  $\tau_{ph}$ . The process then involves an inelastic collision of a phonon of energy (in units of temperature)  $\delta \sim 0.003$  K with an ion which can undergo electronic transitions of  $\Delta \sim 0.05$ ,  $0.15$ , and  $0.25$  K. The interaction must be of second order with the emission or absorption of a second phonon of energy  $\Delta \pm \delta$ . The phonon relaxation time  $\tau_{ph}$  for this process has been derived by Stoneham for ions having two energy levels.<sup>8</sup> Rederiving  $\tau_{ph}$  for the six-level spin system of Pr shown in Fig. 3, insert (ii), we obtain the temperature dependence

$$\mathcal{R}^{-1} = c(a/T) [(e^{a/T} - 1)^{-1} e^{-2a/T} + 27(e^{3a/T} - 1) e^{-a/T} + 125(e^{5a/T} - 1)^{-1}] \left( \sum_{i=0}^5 e^{-ia/T} \right)^{-1} \sim \tau_{ph}^{-1}, \quad (7)$$

where the constant  $c$  is proportional to the concentration of Pr.

Using  $a = 0.05$  K in Eq. (7), the dashed curves of Fig. 4 were obtained. (The finite linewidth of the Pr levels does not significantly change the temperature dependence of these curves.) The fit is rather poor, but the resemblance between the temperature dependence of Eq. (7) and the experimental data of Fig. 4 is nevertheless suggestive that the Pr does, by a two-phonon process, depopulate the phonon band resonant with the Ce. The band of phonons resonant with the Pr transitions are, thus, also distorted from the thermal-equilibrium value. The bottleneck associated with this band of phonons is, by Eq. (2), a factor of  $(\Delta/\delta)^2 \approx 200$  smaller than for the Ce band, and therefore is negligible in these measurements.

A further check on the proposed model is to compare the concentration-dependent parameter  $c$  in Eq. (7) with the data of Fig. 4. This is done in Fig. 5, where  $c^{-1}$  is plotted versus the measured ratio of Pr/Ce. For the samples containing  $1.5 \times 10^{-5}$  or  $5 \times 10^{-6}$  Pr, it was assumed that a temperature-independent relaxation rate operated in parallel with the rate of Eq. (7) to produce the temperature dependencies of Fig. 4. If  $c \propto (\text{Pr/Ce})^n$ , the power  $n$  as found from Fig. 5 is of order unity at low concentration and is less than unity at high concentration. A value  $n = 1$  would be in agreement with the relaxation process of Eq. (7), and  $n < 1$  would be expected for relatively large concentrations. If, in fact,  $n \leq 1$ , it is unlikely that the relaxation of phonons could have been caused by pairs of Pr ions,<sup>36</sup> a process which would produce a somewhat similar temperature dependence in  $\mathcal{R}V$ .

The dependence of  $\tau$  on an externally applied magnetic field would assist in identifying the relaxation

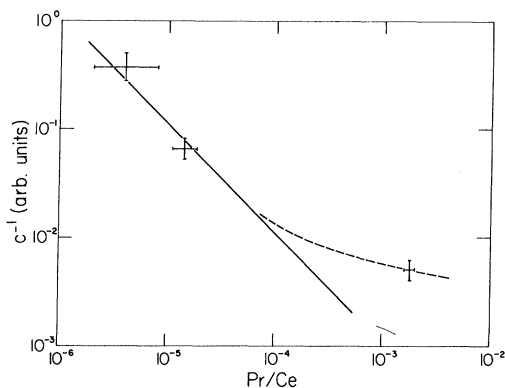


FIG. 5. Values of the concentration-dependent term  $c^{-1}$  from Eq. (7) required to best fit the data of Fig. 4, plotted against the actual Pr concentration of the samples. The solid line represents a linear dependence of  $c$  on Pr concentration.

process, although we have not made such measurements. If the process of Eq. (7) were operative,  $\tau$  should be independent of field<sup>8</sup> up to  $\approx 600$  G. At higher fields the Ce and Pr levels would have the same energy splitting, and the field dependence would become rather complicated.

The decrease in magnetic relaxation time of a crystal upon introduction of Pr impurity has been noted previously, but without elaboration.<sup>12,19</sup> Even the absence of an effect has been noted.<sup>37</sup> Mess also studied the decrease in  $\mathcal{R}$  [Eq. (2)] for CMN containing Cu impurity.<sup>19</sup> The behavior of a Cu-doped sample as a function of temperature and thermal

flux suggested that at higher temperatures the bottleneck was entirely at the interface between sample and bath, as for our samples with  $\text{Pr/Ce} = 8 \times 10^{-3}$ . At low temperatures,  $\mathcal{R}$  for the Cu-doped samples appeared to increase rapidly with decreasing temperature, which is similar to the behavior we observe with Pr-doped CMN.<sup>38</sup>

#### IV. SUMMARY

Evidence has been presented which indicates that the thermal relaxation of  $\text{Ce}^{3+}$  in high-purity crystals of CMN is bottlenecked by the inefficiency of the phonons resonant with the Ce to themselves thermally relax to the bath temperature. The mean free path obtained for these particular phonons would be consistent with other measurements of phonon mean free path in CMN if the phonons resonant with the Ce were somewhat marginally trapped, resonantly, by the Ce. The process is analogous to the resonant trapping of radiation in gases.<sup>39</sup>

It has also been shown that Pr, in effect, breaks the phonon bottleneck. It is very probable that the Pr absorbs those phonons resonant with the Ce by undergoing electronic transitions between hyperfine levels which simultaneously absorb or emit a second phonon of much greater energy. The data are in fair agreement with this model.

If sufficient Pr is added to CMN, the relaxation of the Ce can become dominated by the inability of lattice phonons to thermalize with the bath. The cause of this type of bottleneck is more frequently referred to as the thermal boundary resistance or Kapitza resistance.

<sup>†</sup>Research supported in part by the Advanced Research Projects Agency, under Contract No. HC 15-67-C-0221.

<sup>1</sup>A. Abragam and W. G. Proctor, *Phys. Rev.* **109**, 1441 (1958).

<sup>2</sup>B. W. Faughnan and M. W. P. Strandberg, *Phys. Chem. Solids* **19**, 155 (1961).

<sup>3</sup>J. H. Van Vleck, *Phys. Rev.* **59**, 724 (1941); **59**, 730 (1941).

<sup>4</sup>C. J. Gorter, L. C. Van der Marel, and B. Bolger, *Physica* **21**, 103 (1955).

<sup>5</sup>J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, *Phys. Rev.* **109**, 302 (1958).

<sup>6</sup>P. W. Anderson, *Phys. Rev.* **114**, 1002 (1959).

<sup>7</sup>J. A. Giordmaine and F. R. Nash, *Phys. Rev.* **138**, A1510 (1965).

<sup>8</sup>A. M. Stoneham, *Proc. Phys. Soc. (London)* **86**, 1163 (1965).

<sup>9</sup>H. Glättli, *Can. J. Phys.* **46**, 103 (1968).

<sup>10</sup>V. A. Atsarkin, *Zh. Eksperim. i Teor. Fiz.* **53**, 222 (1967) [*Soviet Phys. JETP* **26**, 149 (1968)].

<sup>11</sup>H. Kalbfleisch, *Phys. Status Solidi* **34**, 685 (1969).

<sup>12</sup>P. L. Scott and C. D. Jeffries, *Phys. Rev.* **127**, 32 (1962).

<sup>13</sup>R. H. Ruby, H. Benoit, and C. D. Jeffries, *Phys. Rev.* **127**, 51 (1962). See also G. H. Larson and C. D. Jeffries, *ibid.* **145**, 311 (1966), for evidence that the

$\text{Ce}^{3+}$  ion interacts predominantly with phonons within the resonance linewidth.

<sup>14</sup>A. R. Miedema and K. W. Mess, *Physica* **30**, 1849 (1964).

<sup>15</sup>J. Wooldridge, *Phys. Rev.* **185**, 602 (1969).

<sup>16</sup>R. C. Mikkelsen and H. J. Stapleton, *Phys. Rev.* **140**, A1968 (1965).

<sup>17</sup>G. H. Larson and C. D. Jeffries, *Phys. Rev.* **141**, 461 (1965).

<sup>18</sup>F. R. Nash, *Phys. Rev.* **138**, A1500 (1965).

<sup>19</sup>K. W. Mess, thesis, Leiden, 1969 (unpublished).

<sup>20</sup>W. J. Brya and P. E. Wagner, *Phys. Rev.* **157**, 400 (1967).

<sup>21</sup>J. E. Robichaux and A. C. Anderson, *Phys. Rev. B* **2**, 5035 (1970). The mean free paths for phonons, as obtained from thermal-conductivity measurements, are of course limited by both elastic and inelastic scattering. They thus serve as a lower limit for comparison with mean free paths appropriate to magnetic relaxation.

<sup>22</sup>S. S. Rifman and P. E. Wagner, *Solid State Commun.* **7**, 453 (1969).

<sup>23</sup>W. B. Mims and D. R. Taylor, *Phys. Rev. Letters* **22**, 1430 (1969). See also R. I. Joseph, D. H. K. Liu, and P. E. Wagner, *ibid.* **25**, 1679 (1968).

<sup>24</sup>S. A. Al'tshuhr, R. M. Valishev, and A. Kh. Klasanov, *Zh. Eksperim. i. Teor. Fiz. Pis'ma v*

Redaktsiyu 10, 179 (1969) [Soviet Phys. JETP Letters 10, 113 (1969)].

<sup>25</sup>W. J. Brya and P. E. Wagner, Phys. Rev. 147, 239 (1966).

<sup>26</sup>Anomalous short  $\tau_d$  have been observed in the ethyl sulfates; see U. Kump, Phys. Status Solidi 34, 691 (1969).

<sup>27</sup>A. C. Anderson, R. E. Peterson, and J. E. Robichaux, Rev. Sci. Instr. 41, 528 (1970).

<sup>28</sup>The rare-earth nitrates were obtained from American Potash and Chemical Corp., Rare Earth Division, West Chicago, Ill. The cerous nitrate was labeled as 99.9999% pure. The magnesium nitrate was obtained from Mallinckrodt Chemical Works, St. Louis, Mo. The final CMN samples, both pure and doped, were analyzed by means of mass and emission spectroscopy. The "pure" samples were found to have a Pr impurity content of  $5 \times 10^{-6}$  ppm atomic, relative to the Ce. There was also a Cu content of  $\sim 5 \times 10^{-5}$  ppm atomic, relative to the Ce.

<sup>29</sup>A. C. Anderson, J. Appl. Phys. 39, 5878 (1968).

<sup>30</sup>W. A. Little, Can. J. Phys. 37, 334 (1959).

<sup>31</sup>A. C. Anderson, G. L. Salinger, and J. C. Wheatley, Rev. Sci. Instr. 32, 1110 (1961); M. Suomi, A. C. Anderson, and B. Holmström, Physica 38, 67 (1968).

<sup>32</sup>A. C. Anderson and R. E. Peterson, Cryogenics 10, 430 (1970).

<sup>33</sup>K. W. Mess, J. Lubbers, L. Niesen, and W. J.

Huiskamp, Physica 41, 260 (1969).

<sup>34</sup>R. P. Hudson and R. S. Kaeser, Physica 3, 95 (1967).

<sup>35</sup>Some difficulty was also encountered in calculating  $\mathcal{R}V$  for the sample containing  $1.8 \times 10^{-3}$  Pr and having a thickness of 0.4 cm. For one datum at 0.07 K, the value of  $\mathcal{R}V$  became negative. Since this could not be plotted on the logarithmic scale of Fig. 4, we averaged all values of  $\mathcal{R}V$  near 0.07 K and plotted the average as the single black point. This is equivalent to drawing a smooth curve through the data of Fig. 2 for the purpose of computing  $\mathcal{R}V$ , rather than using the raw data.

<sup>36</sup>Phonon relaxation by Pr pairs could occur, for example, by simultaneous and opposite spin flips where a phonon of energy  $\delta$  would be absorbed by one ion of the Pr pair undergoing a transition  $\Delta_1$ , the other a transition  $\Delta_2 = \Delta_1 \pm \delta$ , where  $\delta \ll \Delta_{1,2}$ . This is possible in CMN since the dipolar broadening of the Pr lines is  $\approx \delta$ .

<sup>37</sup>J. T. Hoffman and R. C. Sapp, J. Appl. Phys. 39, 837 (1968).

<sup>38</sup>Thus, the improvement or shortening of thermal relaxation times for CMN magnetic thermometers doped with Cu (or Pr) would be lost at sufficiently low temperatures — for example, at  $\sim 0.015$  K for Cu-doped thermometers.

<sup>39</sup>T. Holstein, Phys. Rev. 83, 1159 (1951).

## Isotope Effect for Cation Self-Diffusion in Single Crystals of NiO<sup>†</sup>

M. L. Volpe, N. L. Peterson, and J. Reddy  
Argonne National Laboratory, Argonne, Illinois 60439  
(Received 5 October 1970)

The isotope effect for cation self-diffusion was determined by simultaneous diffusion of <sup>57</sup>Ni and <sup>66</sup>Ni tracers in NiO crystals. The strength of the isotope effect  $f\Delta K$  is  $0.613 \pm 0.021$ , independent of temperature in the range from 1201 to 1678 °C. This result is consistent with cation self-diffusion by a vacancy mechanism only, and  $\Delta K = 0.784 \pm 0.027$ .

### I. INTRODUCTION

In a previous study on the temperature and oxygen-pressure dependence of the transport properties of nickel oxide,<sup>1</sup> we found evidence that self-diffusion occurs predominantly via a vacancy mechanism. One of the objectives of the present investigation was to help establish the mechanism by measuring the isotope effect for cation self-diffusion in this oxide as a function of temperature. This was to be done cooperatively with an isotope-effect study on cation self-diffusion in CoO.<sup>2</sup> By investigating isotope effects in self-diffusion and impurity diffusion in these materials, not only can possible differences in mechanism be detected, but information concerning atomic jump frequencies and their temperature dependence can be obtained.<sup>3</sup> In addition, studies of self-diffusion in dilute solid solutions of these oxides are planned to provide a

test for theories<sup>4</sup> on the effect of solute upon solvent self-diffusion.

It has been well established, both theoretically and by experimental studies on metals, alkali halides, and recently on CoO, that isotope-effect experiments can provide a direct and unequivocal evaluation of the diffusion mechanism. This is so by virtue of the relationship between the experimentally measured isotope effect  $E_\beta$  and the correlation coefficient  $f$ ,<sup>3</sup>

$$E_\beta = \left(1 - \frac{D_\beta}{D_\alpha}\right) / \left[1 - \left(\frac{(n-1)m + m_\alpha}{(n-1)m + m_\beta}\right)^{1/2}\right] \\ = f\Delta K. \quad (1)$$

In Eq. (1),  $f$  depends solely upon the diffusion mechanism and geometrical structure of the diffusion medium. The  $D$ 's are diffusion coefficients for isotopes of mass  $m_\alpha$  and  $m_\beta$ . The number of atoms