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Hyperfine Coupling Temperature Dependence: Mn^{2+} in CaO and SrO

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The effect of temperature variation on the hyperfine coupling constant of Mn^{2+} incorporated in CaO and SrO has been measured by paramagnetic resonance techniques. The experiments were performed on powders and covered the range from room temperature to slightly above 1000°K. These results supplement those of Walsh, Jeener, and Bloembergen, who found a decided explicit (lattice-vibration) dependence for Mn^{2+} in MgO. If an implicit (thermal-expansion) effect similar to the MgO results is assumed for Mn^{2+} in CaO and SrO, they also exhibit a sizeable explicit dependence. Simanek and Orbach have proposed a mechanism in which excited s-like configurations are admixed into the $3d^5$ configuration by the orbit-lattice interaction. Their formula for $A(T)$, which assumes a Debye vibration spectrum, is shown to fit the CaO data very well. The SrO results, showing an extreme linearity compared with MgO and CaO, are anomalous in this context. A modification of the phonon spectrum is suggested as a possible explanation.

I. INTRODUCTION

THE temperature dependence of crystal-field and hyperfine interactions observed in paramagnetic resonance has been examined recently, both experimentally and theoretically, by Walsh, Jeener, and Bloembergen.[1] Their investigation was concerned with iron-group ions which are present as dilute impurities in simple cubic systems, principally magnesium oxide. For this latter host, they observed the effect of temperature upon g shifts in V^{2+} and Cr^{3+}, cubic field splittings of Mn^{2+} and Fe^{3+}, and the hyperfine coupling of $(V^{51})^{2+}$ and $(Mn^{55})^{2+}$. In addition, the hyperfine and cubic-field-splitting temperature dependence of $(Mn^{55})^{2+}$ in ZnS and its hyperfine temperature variation in ZnO, CdTe, and $KMgF_3$ was observed. In all cases but one (ZnS), the crystal-field parameters varied primarily as one would expect from thermal expansion alone. This was shown to be consistent with an effective point-charge model and cubically symmetric lattice vibrations. On the other hand, a decided explicit (lattice vibration) temperature dependence is present in the hyperfine variation. The implicit (thermal expansion) effect is known from pressure experiments[2] to be much smaller and in the opposing sense. Beyond its intrinsic interest, this result has implications for NMR studies of concentrated magnetic materials as pointed out by Walsh *et al.*[1]

A mechanism for the decrease of the Mn^{2+} hyperfine interaction with temperature has been proposed by Simanek and Ohrbach.[3] Excited s configurations, mixed into the $3d^5$ ground configuration by noncubic thermal oscillations, produce a hyperfine field which is opposed to the static (basically core polarization) hyperfine field. The implications of this mechanism were shown to account for the data of Walsh *et al.*[1] on MgO:Mn. It is the purpose of this article to extend the temperature measurements on $(Mn^{55})^{2+}$ to CaO and SrO, and to further test the above mechanism.

II. APPARATUS AND SAMPLES

The EPR measurements were performed at X-band with a high-temperature spectrometer described previ-

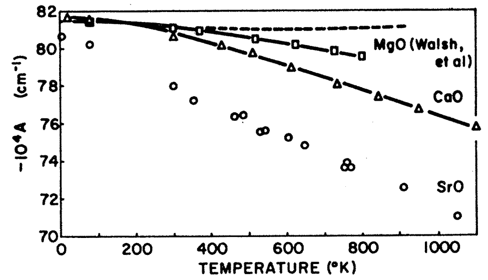

FIG. 1. The variation with temperature of the hyperfine coupling of Mn^{2+} in MgO (from Ref. 1), CaO, and SrO. The dashed curve (Ref. 1) is the implicit effect expected on the basis of pressure experiments. Points designated by □ (MgO) are experimental values for $A(T)$, corrected for thermal expansion, from Ref. 1; those designated by △ (CaO) and ○ (SrO) are uncorrected. The solid lines are calculated from Eq. (1): for MgO, C is $2.58\times10^{-13}(°K)^{-4}$ and $\Theta=750°K$; for CaO, C is $9.01\times10^{-13}(°K)^{-4}$ and $\Theta=650°K$.

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[1] W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965). The reader is referred to this paper for a useful review of the problem and a collection of references to the previous work.

[2] W. M. Walsh, Jr., Phys. Rev. **122**, 762 (1961).

[3] E. Simanek and R. Orbach, Phys. Rev. **145**, 191 (1966).

ously.[4] The samples were off-the-shelf powders which contained sufficient Mn impurity. They were contained in sample vials which left them at atmospheric pressure throughout the measurement. The magnetic field was measured by reference to an NMR-calibrated sweep drive.

III. EXPERIMENTAL RESULTS

Our experimental results for CaO and SrO and those of Walsh *et al.* for MgO are given in Fig. 1. We have also examined MgO in less detail and obtained reasonable agreement with the latter results. Our results cover the range from room to higher temperatures. The data below room temperature were taken from Shuskus[5] for SrO and from Low and Rubins[6] for CaO. We have included the implicit effect expected for MgO on the basis of pressure experiments as given by Walsh *et al.*[1] in order to show the predominance of the explicit temperature dependence. Since no such pressure data exist for CaO and SrO, it is not possible to correct for thermal expansion. However, there is no *a priori* reason to expect an anomaly in either of these cases, and we shall assume for now that all the data in Fig. 1 show closely the explicit dependence.

IV. DISCUSSION

A fundamental approach to explain the observed hyperfine temperature variation is offered in the work of Simanek and Orbach.[3] If excited configurations of the form $3d^4ns$ are admixed into the ground $3d^5$ configuration by phonon-induced noncubic fields, the admixed s states will have spin parallel to the spin of the ground state. This is so since the induced field is electric in character. It is known, however, that the hyperfine coupling in the ground configuration arises primarily from core polarization[7] which produces a hyperfine field opposed in sign to that of an s electron with the same spin direction as this configuration. Thus, the net decrease of A from the $T=0$ value is readily explained.

The results of the calculation by Simanek and Orbach are twofold. First, using a Debye model for the lattice vibrations, the actual form of the temperature dependence is derived:

$$A(T)=A(0)\left[1-CT^4\int_0^{\Theta/T}\frac{x^3dx}{(e^x-1)}\right], \qquad (1)$$

where Θ is the averaged Debye temperature and C, although complicated, is given explicitly in terms of theoretical quantities appropriate to a near-neighbor point-charge model. When C is treated as an adjustable parameter, this equation for $A(T)$ is shown to fit the experimental data very well for MgO:Mn, which has been corrected for thermal expansion, with a value of $C=2.58\times10^{-13}(°\mathrm{K})^{-4}$. A value of $\Theta=750°\mathrm{K}$, obtained from low-temperature specific-heat data, was assumed. The value of C calculated on the point-ion model is an order of magnitude too small; however, Simanek and Huang[8] have recently recalculated C taking covalency into account, and have obtained $C=2.16\times10^{-13}(°\mathrm{K})^{-4}$ in good agreement with experiment.

The data presented here may also be fit to Eq. (1) if we assume that the correction for thermal expansion is relatively small. If pressure-dependent measurements become available, a minor correction may be made. Unlike the case of MgO, no values of the Debye temperature for either CaO or SrO are available, to the best of our knowledge. This compels us then to treat Eq. (1) as a two-parameter equation which, of course, weakens somewhat the use of our data to test this equation. However, we do not consider this to be serious since the integral is not a very sensitive function of Θ in the range of any reasonable values of this quantity. We have made a least-squares fit of our CaO data to Eq. (1) for a set of values of Θ and find that the smallest mean square deviation occurs for $\Theta=650°\mathrm{K}$ with a corresponding value of $C=9.01\times10^{-13}(°\mathrm{K})^{-4}$ and $-A(0)$ -81.59×10^{-4} cm^{-1}. If we use this technique with the corrected data of Walsh *et al.*[1] for MgO, we require $\Theta=850°\mathrm{K}$ and find $C=2.18\times10^{-13}(°\mathrm{K})^{-4}$ with $-A(0)=81.46\times10^{-4}$ cm^{-1}. The theoretical curves which best fit the data for MgO and CaO are presented in Fig. 1. For CaO as well as MgO, a good fit is obtained with reasonable values of the parameters. Referring to the experimental points for SrO, the linearity appears to extend well into the low-temperature region. There are only two points available below 300°K upon which to base this observation, and, in fact, the slope should be zero for $T=0$ (as observed for MgO and CaO) since the lattice modes "freeze out" at low temperature. Nevertheless, it appears from the available data that the turning point in the curve occurs at such a low temperature that Eq. (1) could only be satisfied with an unreasonably low Debye temperature. For this reason we have not shown a theoretical curve for SrO in Fig. 1.

A possible alternative explanation for the SrO data involves a modification of the phonon spectrum from the Debye spectrum assumed in Ref. 3. The linearity of $A(T)$ for SrO at low temperatures could be accounted for by a low-frequency resonance mode in which the neighbors of the impurity move with large amplitude[9,10] (Mills[11] has demonstrated the importance of such modes

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[4] L. Yarmus, M. Kukk, and B. R. Sundheim, J. Chem. Phys. **40**, 33 (1964).

[5] A. Shuskus, J. Chem. Phys. **41**, 1885 (1964).

[6] W. Low and R. S. Rubins, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963).

[7] For an extensive review of hyperfine interactions, see A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA.

[8] E. Simanek and N. L. Huang, Phys. Rev. Letters **17**, 698 (1966).

[9] R. Brout and W. Visscher, Phys. Rev. Letters **9**, 54 (1962).

[10] A. A. Maradudin, Rept. Progr. Phys. **28**, 331 (1965) (see especially p. 357).

[11] D. L. Mills, Phys. Rev. **146**, 336 (1966).

in a related context, that of spin-lattice relaxation). The Simanek-Orbach mechanism requires a noncubic mode of even inversion symmetry. A low-frequency resonance mode of the required symmetry could result from a reduction of the force constant accompanying the impurity; such a reduction is reasonable in that the lattice constant is substantially larger for SrO than for MnO. The impurity ion is stationary in a mode of even symmetry, and consequently there is no longer a distinction between strain and displacement of neighboring ions; thus, Eqs. (16) and (17) of Ref. 1 can be adapted to give a hyperfine temperature dependence of the form

$$A(T)=A_0+(A_1/\omega)\coth(\hbar\omega/2kT). \quad (2)$$

The form of Eq. (2) is reasonable in that it is linear in T for high temperature ($\hbar\omega \ll kT$) and independent of T for very low temperature ($\hbar\omega \gg kT$). A proper test of this speculation would require additional low-temperature data. In fact, the choice between the alternative phonon spectra could be made only on the basis of a detailed investigation of $A(T)$ at low temperatures. The low-temperature form of Eq. (1) is

$$A(T)=A_0[1-\pi^4CT^4/15], \quad (3)$$

and that of Eq. (2) is

$$A(T)=A_0+2(A_1/\omega)\exp(-\hbar\omega/kT). \quad (4)$$

Finally, correction for thermal expansion might cause the SrO results to appear more reasonable although it would be difficult to explain this. In any case there is a clear need now to round out these results with pressure measurements for CaO and SrO in addition to detailed low-temperature measurements.

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Rare-Earth–Iron Exchange Interactions in Europium Iron Garnet

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Recoilless absorption measurements of the 14.4-keV γ rays of Fe^{57} and the 21.6-keV γ rays of Eu^{151} in europium iron-gallium garnets ($Eu_3Ga_xFe_{5-x}O_{12}$) were carried out at 4.2°K for $x=0$, 0.66, 1.28, 1.60, 2.37, and 3.03. The iron concentrations in the octahedral and tetrahedral sites were determined from the Fe^{57} spectra. The results show that about 80% of the Ga ions occupy tetrahedral sites (~85% for $x=0.66$ and ~75% for $x=3.03$). The analysis of the Eu^{151} spectra shows that $(88\pm4)\%$ of the exchange field acting on an Eu^{3+} ion in europium iron garnet is produced by the two nearest iron neighbors in the tetrahedral site, although the Eu-O-Fe angle for these ions is 92°, an angle often considered unfavorable for superexchange interactions. Excellent agreement between theoretical and experimental spectra is obtained assuming that the remaining 12% of the exchange field is produced by the 4 third nearest neighbors in the tetrahedral site.

INTRODUCTION

The main purpose of the present work was to study the rare-earth–iron exchange interactions in rare-earth–iron garnets and specifically the contributions of the various iron neighbors to the exchange field acting on a rare-earth ion in the garnets. The gallium-substituted europium iron garnet ($Eu_3Ga_xFe_{5-x}O_{12}$) system has the following advantages for the study of rare-earth–iron exchange interactions: (1) The magnitude of the magnetic hyperfine field ($H_{\rm eff}$) acting on an Eu nucleus of an Eu^{3+} ion is very sensitive to the value of the exchange field ($H_{\rm exch}$) acting on the ion. As explained in the next section, $H_{\rm eff}$ is approximately proportional to $H_{\rm exch}$ in ferrimagnetic compounds of europium. For any other rare-earth ion, the value of $H_{\rm eff}$ at magnetic saturation is almost independent of $H_{\rm exch}$. (2) Well-resolved lines are obtained in the absorption spectra of the 21.6-keV γ rays of Eu^{151} in ferrimagnetic compounds of europium. (3) The Ga^{3+} ions strongly prefer the tetrahedral sites of the garnet and, therefore, by changing x, the relative concentrations of the iron ions in the tetrahedral and octahedral sites change. The hyperfine spectra are very sensitive to the value of x and from the analysis of the spectra obtained for absorbers with various values of x, it is possible to draw conclusions concerning the contributions of the various neighbors of an Eu^{3+} ion to the exchange field acting on it.

The crystal structure of the garnets has been dis-

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