

Sign of the Nearest-Neighbor Exchange Interaction and its Derivative in GdAs*

E. D. JONES AND B. MOROSIN

Sandia Laboratory, Albuquerque, New Mexico

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The sign of the nearest-neighbor exchange interaction J_1 and its logarithmic derivative $\partial \ln J_1 / \partial r$ has been determined for the intermetallic type-II antiferromagnet GdAs. The As⁷⁶ nuclear-magnetic-resonance Knight-shift data in the paramagnetic state of GdAs were used to yield a value for the Curie-Weiss temperature $\theta \approx -35^\circ\text{K}$. Combining this value with the Néel temperature $T_N \approx 25^\circ\text{K}$ and using the molecular field theory gives $J_1 = -0.08^\circ\text{K}$ and $J_2 = -0.40^\circ\text{K}$. The measurement of the sign of $\partial \ln J_1 / \partial r$ in GdAs was performed using low-temperature x-ray powder-diffraction techniques in order to study the exchange-striction-induced trigonal lattice distortion for $T < T_N$. The observed trigonal distortion was found to be a compression along the [111] direction of the NaCl-type GdAs crystal structure. From the sign of the trigonal distortion, it is concluded that $\partial \ln J_1 / \partial r$ is negative. Similar data for GdP suggest that $\partial \ln J_1 / \partial r$ is also negative for this compound.

I. INTRODUCTION

ANY model for the origin of exchange interactions between magnetic moments in solids requires a knowledge of the signs and magnitudes of these interactions and their derivatives with respect to distance before quantitative predictions concerning the magnetic properties can be made. In general, only information about exchange interactions can be obtained from the type of magnetic order, ordering temperature, and Curie-Weiss temperature. However, information concerning the sign of $\partial \ln J / \partial r$ (the logarithmic derivative of the exchange constant J with respect to distance r) is usually difficult to obtain because of the inter-relationship between all of the exchange interactions which contribute to a physical measurement. For example, a measurement of the pressure dependence of the Curie-Weiss temperature contains contributions from all of the exchange energies. Hence, separating the individual contributions from each exchange energy to the pressure dependence is usually difficult. An alternate method for determining the signs of some of these derivatives is the use of x-ray powder-diffraction measurements in the ordered state of the compound under study if the magnetic structure is known. The x-ray diffraction method allows a determination of the sign of $J \partial \ln J / \partial r$ from a study of the effects of exchange striction on the lattice symmetry of the magnetic compound under study. Hence, from a knowledge of the sign of J and the sign of the exchange-striction-induced lattice distortion, the sign of $\partial \ln J / \partial r$ can be inferred. The x-ray diffraction technique is limited to a few special cases where the type of magnetic order has the correct symmetry; where the exchange striction can unambiguously be attributed to a single exchange constant.

This paper will present and discuss the results of nuclear magnetic resonance (NMR) and low-temperature x-ray powder-diffraction measurements in GdP

and GdAs. It will be shown that an interpretation of the NMR data yields different signs for the nearest-neighbor exchange interaction J_1 for both GdP and GdAs from those determined from paramagnetic susceptibility measurements.^{1,2} An interpretation of the x-ray diffraction measurements gives $\partial \ln J_1 / \partial r < 0$ for these compounds.

The experimental apparatus and techniques are briefly described in Sec. II. Section III presents and discusses the NMR data in GdP and GdAs. The resulting exchange interactions which are deduced from the NMR data in GdP and GdAs are also contained in Sec. III. Section IV contains the x-ray diffraction measurements.

II. EXPERIMENTAL

The phosphorus and arsenic NMR were observed in powdered samples of GdP and GdAs between 100° and 600°K using a variable frequency spectrometer and a conventional laboratory electromagnet. Sample temperatures were obtained using a calibrated variable-temperature unit. The phosphorus and arsenic Knight-shift measurements were made at a fixed frequency, by measuring the resonant magnetic field with respect to red phosphorus for GdP and the aluminum NMR in a saturated solution of Al₂(SO₄)₃ for GdAs. The phosphorus and arsenic Knight shifts were found to be field-independent between 2 and 16 Mc/sec.

The x-ray powder measurements on GdP and GdAs were made using Cu $K\alpha$ radiation and a 114.5 mm Norelco powder camera. The low-temperature lattice constants were obtained with an x-ray diffraction cryostat described elsewhere.³

The GdP and GdAs samples were prepared by mixing appropriate amounts of gadolinium and phosphorus or arsenic and heating to 600°C for several days. Exami-

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² G. Busch, O. Vogt, and F. Hulliger, *Phys. Letters* **15**, 301 (1965).

³ B. Morosin, *J. Chem. Phys.* **44**, 252 (1966).

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TABLE I. Exchange energies, Néel, and Curie-Weiss temperatures obtained from paramagnetic susceptibility and NMR measurements. All data are in units of °K.

| | T_N | θ | Paramagnetic susceptibility ^a | | θ | NMR | |
|------|-------|----------|--|-------|----------|-------|-------|
| | | | J_1 | J_2 | | J_1 | J_2 |
| GdP | 15 | 0 | +0.12 | -0.24 | -25 | -0.08 | -0.24 |
| GdAs | 25 | -12 | +0.10 | -0.40 | -35 | -0.08 | -0.40 |

^a References 1 and 2.

nation of the resulting GdP and GdAs compounds by standard x-ray powder techniques verified that the samples had the correct NaCl-type crystal structure.

III. PHOSPHORUS AND ARSENIC NMR IN GdP AND GdAs

Neutron diffraction,⁴ magnetization and paramagnetic susceptibility measurements⁵⁻⁹ have been performed on a large number of the intermetallic rare-earth group VA NaCl-type compounds. Recently, experimental determinations of the Néel temperature T_N and Curie-Weiss temperature θ for the type-II fcc antiferromagnets GdP¹ and GdAs² have been used to evaluate the nearest-neighbor (nn) and next-nearest-neighbor (nnn) exchange interactions J_1 and J_2 . Using molecular field theory, the resulting exchange interactions were found^{1,2} to be $J_1 = +0.12^\circ\text{K}$, $J_2 = -0.24^\circ\text{K}$ for GdP and $J_1 = +0.10^\circ\text{K}$, $J_2 = -0.40^\circ\text{K}$ for GdAs. These results together with the Néel and Curie-Weiss temperatures are summarized in Table I.

The theory and underlying principles of NMR measurements in rare-earth intermetallic compounds will not be discussed here, since the subject has been adequately treated in the literature.¹⁰ For the purposes of this paper, it is sufficient to state that the phosphorus or arsenic Knight shift in the paramagnetic state of GdP or GdAs can be written as¹¹

$$K(T) = K_0 + (N\beta)^{-1} H_{\text{hf}} \chi(T), \quad (1)$$

where $K(T)$ is the total temperature-dependent Knight shift, K_0 is the measured¹² Knight shift in the nonmagnetic isomorphs LaP ($K_0 \approx 0.06\%$) and LaAs ($K_0 \approx 0.14\%$), N is Avogadro's number, β is the Bohr magneton, H_{hf} is the total phosphorus or arsenic nuclear

hyperfine field per Bohr magneton and $\chi(T)$ is the gadolinium spin susceptibility expressed in emu/mole. Since the gadolinium spin susceptibility $\chi(T)$ obeys a Curie-Weiss law, Eq. (1) can be rewritten as

$$K(T) = K_0 + H_{\text{hf}} C [N\beta(T - \theta)]^{-1}, \quad (2)$$

where $C = 7.88$ (emu-°K/mole), the expected Curie-Weiss constant for the Gd³⁺ ion.

Thus, by plotting the observed $[K(T) - K_0]^{-1}$ versus temperature for GdP and GdAs, the Curie-Weiss temperature θ can be determined. Also, information regarding the size and magnitude of the hyperfine field H_{hf} can be obtained from such a graph. However these results will be presented elsewhere,¹³ together with the NMR data for most of the rare-earth group VA compounds.

Figure 1 shows the results of plotting the observed $[K(T) - K_0]^{-1}$ versus temperature for the phosphorus and arsenic NMR data in GdP and GdAs between 100 and 600°K. The sign of the ordinate in Fig. 1 indicates that the observed phosphorus and arsenic Knight shifts in GdP and GdAs are negative. Extrapolating the NMR data to zero ordinate gives $\theta = -25^\circ\text{K}$ for GdP and $\theta = -35^\circ\text{K}$ for GdAs.

In the molecular-field approximation, assuming that there are only nn and nnn exchange interactions J_1 and J_2 , the Néel and Curie-Weiss temperatures T_N and θ are given by¹⁴

$$T_N = -4J_2 S(S+1), \quad (3)$$

and

$$T_N + \theta = 8J_1 S(S+1), \quad (4)$$

where $S (= \frac{7}{2})$ is the Gd³⁺ spin and the exchange energies J_1 and J_2 are in units of °K. Using the above determined NMR values for the Curie-Weiss temperatures, Eqs. (3) and (4) give $J_1 = -0.08^\circ\text{K}$, $J_2 = -0.24^\circ\text{K}$ for GdP and $J_1 = -0.08^\circ\text{K}$, $J_2 = -0.40^\circ\text{K}$ for GdAs. These results are summarized in Table I.

It is evident from Table I, that there is a significant difference between the signs of the nn exchange interactions J_1 obtained from the paramagnetic susceptibility^{1,2} and NMR measurements. The determination of the sign of J_1 depends critically upon the value of the Curie-Weiss temperature used in Eq. (4). The differences between the NMR- and paramagnetic-susceptibility-determined exchange interactions are thus reflected in the differences in the Curie-Weiss temperatures. The probable reason for these differences for the value of θ is the fact that the NMR technique observes only the compound of interest, while the paramagnetic susceptibility measurement is a bulk measurement. Hence, a measurement of the paramagnetic susceptibility is dependent upon the purity of the sample, while the NMR technique is generally rather

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⁵ G. Busch, P. Junod, O. Vogt, and F. Hulliger, Phys. Letters **6**, 79 (1963).

⁶ G. Busch, O. Marínček, A. Menth, and O. Vogt, Phys. Letters **14**, 262 (1965).

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⁸ T. Tsuchida and W. E. Wallace, J. Chem. Phys. **43**, 2087 (1965).

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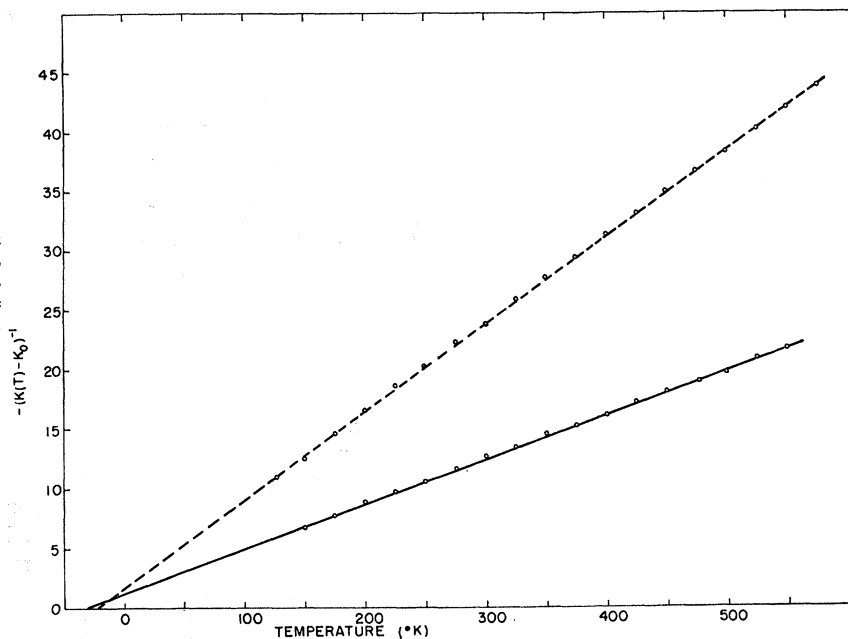
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¹³ E. D. Jones (to be published).

¹⁴ J. S. Smart, *Magnetism III*, edited by G. Rado and H. Shul (Academic Press Inc., New York, 1963).

FIG. 1. The phosphorus and arsenic Knight shifts $K(T)$ in GdP and GdAs between 100 and 600°K are plotted as $[K(T) - K_0]^{-1}$ versus temperature. The dashed line is data for GdP and the solid line is data for GdAs.



insensitive to small amounts of any impurities, e.g., Gd_2O_3 . Including an experimental error of about $0.1K(T)$ in the Knight-shift measurements, the NMR-determined Curie-Weiss temperatures given in Table I have an error of about $\pm 10\%$. This error for the Curie-Weiss temperature will not affect the sign of the nn exchange interaction J_1 , i.e., it remains negative.

IV. X-RAY DIFFRACTION STUDIES IN GdP AND GdAs

For the type-II fcc antiferromagnetic compounds, x-ray powder-diffraction measurements of the exchange-striction-induced trigonal distortion of the lattice in the ordered state allows a direct determination of the sign of the product $J_1 \partial \ln J_1 / \partial r$. Previously,¹⁵ this technique has been restricted primarily to the study of the temperature dependence of the trigonal distortion in the type-II fcc antiferromagnets MnO and NiO. Briefly, the exchange-striction process in these antiferromagnetic compounds proceeds as follows. The type-II magnetic order consists of ferromagnetically aligned sheets of spins lying in (111) planes, and the spin directions of these sheets are arranged antiferromagnetically from plane to plane. Around a given magnetic spin, there are twelve nearest neighbors; six parallel and six antiparallel. The six parallel nn spins are located in the same ferromagnetic sheet as the reference spin, with three of the antiparallel nn spins in the plane above and the remaining three antiparallel nn spins in the plane below. When the nn exchange interaction J_1 is antiferromagnetic (negative) and if the exchange interaction decreases with increasing

separation between the magnetic spins, i.e., $\partial \ln J_1 / \partial r < 0$, the system (magnetic plus elastic) will lower its energy by contracting along a [111] direction. For the case of a positive $\partial \ln J_1 / \partial r$, the system will energetically favor an expansion along the [111] direction. In either case, six of the nn spins will decrease and six will increase their separation from the reference spin.

Let the deformed cube have corner angles $\frac{1}{2}\pi \pm \Delta$. For a small trigonal distortion, the resulting equilibrium angle Δ_{eq} is given by¹⁵

$$\Delta_{\text{eq}} = -Nz_1 J_1 \epsilon \langle S \rangle^2 / 2C, \quad (5)$$

and

$$\epsilon = -r(\partial \ln J_1) / \partial r, \quad (6)$$

where $z_1 (=12)$ is the number of nearest neighbors of any particular spin, N is the number of spins in the system, $\langle S \rangle$ is the time-averaged value of the gadolinium spin, and $C (=3C_{44})$ is the appropriate elastic constant. For a compression along the [111] direction Δ_{eq} is positive and for an expansion Δ_{eq} is negative.

Thus by performing x-ray diffraction measurements in the ordered state of GdP and GdAs, the sign of $\partial \ln J_1 / \partial r$ can be determined from the type of trigonal distortion that the lattice undergoes since the sign of J_1 is also known.

At this point it is worth mentioning why the logarithmic derivative $\partial \ln J_1 / \partial r$ has been used in Eqs. (5) and (6) instead of $\partial J_1 / \partial r$. For the type-II antiferromagnet, J_1 can, under the proper condition, be positive or negative. Hence, the sign of $\partial J_1 / \partial r$ depends upon the sign of J_1 . Thus a sign for $\partial J_1 / \partial r$ can be confusing, i.e., for J_1 negative, $\partial J_1 / \partial r > 0$ means that the exchange energy becomes larger as r decreases while for the case

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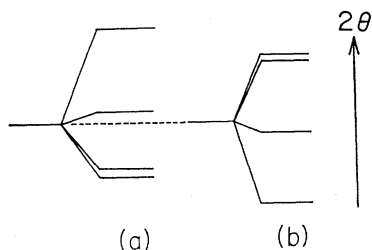


FIG. 2. A schematic of the splitting for the (642) x-ray powder diffraction line due to a small trigonal distortion. Part (a) is for the case of a compression and part (b) is for an expansion along the threefold axis. Increasing 2θ is denoted by the arrow in the figure.

of J_1 positive, $\partial J_1/\partial r > 0$ means that the exchange energy decreases with decreasing r . In an attempt to make the situation clearer, the logarithmic derivative $\partial \ln J_1/\partial r$ has been used. Thus, $\partial \ln J_1/\partial r$ is independent of the sign of J_1 and $\partial \ln J_1/\partial r < 0$ unambiguously means that the exchange energy increases with decreasing r .

Theoretically,¹⁵⁻¹⁸ it is possible to obtain also the magnitude of $\partial \ln J_1/\partial r$ from the size of the trigonal distortion. However, in order to perform the calculation for $\partial \ln J_1/\partial r$, knowledge of the appropriate elastic constants is required [see Eq. (5)].

The effect of exchange-striction-induced lattice distortion by the antiferromagnetic nnn exchange interaction J_2 in a type-II fcc antiferromagnet is to cause a volume distortion of the lattice. The effect of a third-nearest-neighbor exchange interaction J_3 (if it exists) does not give rise to a simply describable lattice distortion. In general, it is easy to show that for the type-II fcc antiferromagnet, *only* the nn exchange interaction J_1 will cause a pure trigonal distortion of the lattice. The effects of including biquadratic exchange have not been considered in the analysis of the exchange-striction process for two reasons; (1) it is presently thought that biquadratic exchange is relatively unimportant in the exchange-striction process, and (2) there seems to be some question on how to include correctly the effects of biquadratic exchange in Eq. (5).

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¹⁷ J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 197 (1957).

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¹⁹ A. Iandelli, *Rare Earth Research*, edited by V. Kleber (The Macmillan Company, New York, 1961).

Room temperature ($23 \pm 1^\circ\text{C}$) lattice parameters for GdP and GdAs were determined, using Cu $K\alpha$ radiation, to be (5.7286 ± 0.0003) Å for GdP and (5.8656 ± 0.0004) Å for GdAs. These values for the lattice constants are in good agreement with previously published data.¹⁹ The GdP and GdAs lattice constants were found to obey a linear relationship with respect to temperature between 30 and 300°K . The linear thermal coefficients of expansion for this temperature range were measured to be $(5.9 \pm 0.4) \times 10^{-6} (\text{°K})^{-1}$ for GdP and $(7.1 \pm 0.5) \times 10^{-6} (\text{°K})^{-1}$ for GdAs. It is interesting to note that these values for the thermal coefficient of expansion are typical of those found for metals.

At a temperature of 5°K , a small splitting of the highest 2θ line [corresponding to the (642) reflection] was noted for GdAs, while the (640) reflection for GdP was broadened. The expected splitting of the (642) powder x-ray spectrum because of a small trigonal distortion is shown in Fig. 2. Figures 2(a) and 2(b) are the schematic representations of the powder spectrum corresponding to a compression, and to an expansion along the threefold axis. Although the distortion from cubic symmetry for GdAs was very small, it allowed the direct observation that the unit cell is *compressed* along the threefold axis. The resulting GdAs lattice parameters at 5°K are $a_0 = (5.8541 \pm 0.0006)$ Å and $\alpha = (90.034 \pm 0.007)^\circ$. For GdP at 5°K , $a_0 = (5.7194 \pm 0.0006)$ Å and an upper limit to the distortion was estimated to be $\alpha = 90. + \delta$ with $\delta \leq 0.007^\circ$.

The observed compression along the GdAs threefold axis for $T < T_N$ is thus a measurement of the sign of $\partial \ln J_1/\partial r$. For GdAs, it is therefore concluded that $\partial \ln J_1/\partial r$ is negative, i.e., $|J_1|$ increases as r decreases.

Although there was no discernible splitting observed for the (640) reflection in GdP, it is at this point tentatively concluded that GdP probably undergoes a similar type of trigonal distortion as observed in GdAs.

It is worth re-emphasizing that for the proper magnetic symmetry, the x-ray diffraction study of an exchange-striction-induced lattice distortion can yield information regarding the sign of $J\partial \ln J/\partial r$.

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