PHYSICAL REVIEW B VOLUME 8, NUMBER 12 15 DECEMBER 1973

Crystal Fields and the Effective-Point-Charge Model in the Rare-Earth Pnictides

R. J. Birgeneau,* E. Bucher, and J. P. Maita
Bell Laboratories, Murray Hill, New Jersey 07974

L. Passell
Brookhaven National Laboratory,† *Upton, New York 11973*

K. C. Turberfield*
Atomic Energy Research Establishment, Harwell, England

(Received 19 June 1973)

Neutron scattering and specific-heat studies of the crystal fields in the rare-earth monophosphides are reported. It is found that the fourth-order crystal-field parameters for the phosphides and for other rare-earth pnictides fall on a universal curve which is close to that predicted by an effective-point-charge model for the light rare earths but deviates markedly for the heavy rare earths.

Crystal-field effects in insulators have been the subject of intense research for more than four decades. The corresponding problem in metals, however, has only been seriously studied in the last few years. This recent interest in crystal fields in metals has been stimulated especially by two important experimental advances: (i) it has been found that inelastic-neutron-scattering techniques can yield detailed information about the crystal fields in a large class of rare-earth metallic compounds,[1–5] (ii) electron-paramagnetic-resonance studies of very dilute noble-metal–rare-earth and transition-metal–rare-earth alloys have yielded precise information about the crystal fields seen by the rare-earth impurities.[6] The theory of crystal fields in metals, however, is still in its early stages of development. In some systems, notably the noble-metal dilute alloys, the conduction electrons seem to play a dominant role in determining the magnitude and sign of the crystal field,[7] whereas in others, such as the praseodymium monopnictides and monochalcogenides, a simple effective-point-charge model (EPCM) which omits the conduction electrons entirely seems to be completely adequate.[2] At this stage it seems clear that systematic studies of crystal fields over a range of compounds are essential for our understanding of the microscopic origins of the crystal fields in metals. Accordingly, we have carried out a detailed inelastic-neutron-scattering study of crystal-field spectra across the complete rare-earth monophosphide series. Specific-heat measurements have also been performed on LaP, LuP, LaSb, LuSb, SmP, and SmSb as a supplement to the neutron scattering studies. As we shall see, our experiments show that the crystal fields in this class of metallic compounds exhibit remarkably simple behavior.

The crystal-field Hamiltonian for the O_h symmetry appropriate to the rare-earth-monopnictide rocksalt structure may be written

$$\mathcal{H}_{\mathrm{CEF}} = A_4\langle r^4\rangle\chi_4[O_4^0(J)+5O_4^4(J)] + A_6\langle r^6\rangle\chi_6[O_6^0(J)-21O_6^4(J)], \qquad (1)$$

where the O_n^m are the usual Stevens-operator equivalents and the χ_n are reduced matrix elements.[8] In the EPCM, the crystalline-electric-field (CEF) coefficients $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$ are given simply by

$$\begin{aligned} A_4\langle r^4\rangle &= \tfrac{7}{16}(Ze^2/R_{nn}^5)\langle r^4\rangle(1+\epsilon_4), \\ A_6\langle r^6\rangle &= \tfrac{3}{64}(Ze^2/R_{nn}^7)\langle r^6\rangle(1+\epsilon_6), \end{aligned} \qquad (2)$$

where Ze is the effective charge at the ligand, R_{nn} is the rare-earth-ligand separation, and ϵ_4, ϵ_6 are small correction factors to allow for the effect of more-distant neighbors. In this case, we estimate $\epsilon_4 \sim 0.06$, $\epsilon_6 \sim 0.14$ so that we shall take them to be effectively zero. Our previous experiments[2] on PrP, PrAs, PrSb, PrBi, PrS, PrSe, and PrTe showed that quantitative agreement for all compounds could be obtained from (2) with $ZE = -2$ and $\langle r^n\rangle$ is equal to the nonrelativistic Freeman-Watson values.[9] This was particularly surprising since the conduction-electron concentrations were markedly different in the pnictides and chalcogenides. More recently, Davis and Mook[5] have presented results for PrN, and they have made two important observations: (i) PrN has $Ze = -3$, implying that the nitrides are fundamentally different from the other pnictides; (ii) it is necessary to use relativistic values[10] for the $\langle r^n\rangle$. For PrP this implies $Ze \sim -1.2$, if one uses the Dirac-Slater values calculated by Lewis.[10] The PrX experiments have, however, confirmed the R_{nn}^{-5} EPCM prediction for $A_4\langle r^4\rangle$; by studying the rare-earth-phosphide series, we should be able to probe the $\langle r^n\rangle$ dependence in Eq. (2).

The neutron scattering experiments were performed on the "slow-chopper" neutron time-of-flight spectrometer at the Brookhaven high-flux-

TABLE I. Crystal-field parameters in the rare-earth monophosphides.

Compound with number of $4f$ electrons	Lattice constant (Å)	$A_4\langle r^4\rangle$ (meV)	$A_6\langle r^6\rangle$ (meV)
CeP($4f^1$)	5.942	5.5 ± 1	
PrP($4f^2$)	5.905	13.8 ± 0.7	0.37 ± 0.2
NdP($4f^3$)	5.863	11.4 ± 0.6	0.69 ± 0.20
SmP ($4f^5$)	5.780	8.9 ± 0.3	•••
TbP($4f^8$)	5.685	6.4 ± 1.0	0 ± 1.0
HoP($4f^{10}$)	5.627	9.5 ± 0.5	0.34 ± 0.2
ErP($4f^{11}$)	5.599	11.3 ± 0.6	0.35 ± 0.2
TmP($4f^{12}$)	5.572	9.0 ± 0.4	0.51 ± 0.2
YbP($4f^{13}$)	5.550	8.9 ± 0.4	1.2 ± 0.6

beam reactor. The characteristics of this instrument and the details of the experimental method and analysis have been discussed at length previously[2,3] so we will not reproduce these here. Experiments were performed on CeP, NdP, HoP, ErP, TmP, and YbP, the other rare earths having prohibitively large neutron absorption cross sections. Spectra were taken typically at 295, 77, and 4.2 K, although where necessary data were obtained at several additional temperatures. We have previously presented data for PrP. Similar spectra are observed for the other rare-earth phosphides listed above. In all cases, a sufficiently large number of transitions are observed to determine the CEF parameters uniquely. In general, the spectra can be accounted for in detail using the eigenvalues and eigenfunctions determined from the diagonalization of Eq. (1) with the appropriate values for $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$. The widths of the transitions are typically less than 1 meV, thus indicating that the exchange energies are significantly less than the crystal-field energies in these materials. The final CEF parameters obtained by least-squares fits to the spectra are listed in Table I.

Specific-heat measurements were performed on six of the pnictides, LaP, LuP, SmP, LaSb, LuSb, SmSb between 1.7 and 45 K using the Morin-Maita heat-pulse technique.[11] The results for the La and Lu compounds are listed in Table II. It is interesting to note that the electronic specific heats are essentially the same for all pnictide compounds thus indicating closely similar electronic properties. We note also that the pnictide γ's are considerably reduced from those in the corresponding chalcogenides, where $\gamma \simeq 4$ mJ/K^2 formula unit,[12] as expected on the basis of simple valence arguments. In a cubic crystal field, the Sm^{3+} $J=\frac{5}{2}$ ground-state manifold is split into a Γ_7 doublet and Γ_8 quartet. The parameter $A_4\langle r^4\rangle$ thus can simply be deduced from a measurement of the Γ_7-Γ_8 splitting via its Schottky specific-heat anomaly. After subtraction of the appropriate lattice and electronic components estimated via the La, Lu compounds, the residual specific heats in SmP, SmSb are indeed found to correspond to Schottky anomalies originating from fourfold-degenerate excited states at energies of 93 and 65 K, respectively. These energies correspond to CEF parameters $A_4\langle r^4\rangle(\mathrm{SmP}) = 8.9 \pm 0.3$ meV, $A_4\langle r^4\rangle(\mathrm{SmSb}) = 5.7 \pm 0.2$ meV.

TABLE II. Low-temperature thermodynamic parameters for some Lu^{3+} monopnictides.

Compound	γ (mJ/K^2 formula unit)	$\Theta_D(0)$ (K)
LaP	0.80 ± 0.1	299 ± 6
LuP	0.83 ± 0.1	346 ± 6
LaSb	0.8 ± 0.1	225 ± 4
LuSb	0.9 ± 0.1	241 ± 4

We now consider the experimental results tabulated in Table I and displayed in Fig. 1. It is evident that the crystal field is always predominantly fourth order. In Fig. 1 we plot $A_4\langle r^4\rangle$ multiplied by the lattice constant a raised to the fifth power [cf. Eq. (2)] both for the phosphides and for all other pnictides which have been studied spectroscopically.[1-4] We have deliberately omitted PrN since as noted by Davis and Mook,[5] the nitrides, unlike the other pnictides, are probably semiconductors and hence should exhibit quantitatively different crystal fields. It is evident that the cerium compounds are all anomalous. This anomalous behavior assumedly originates in the proximity of the

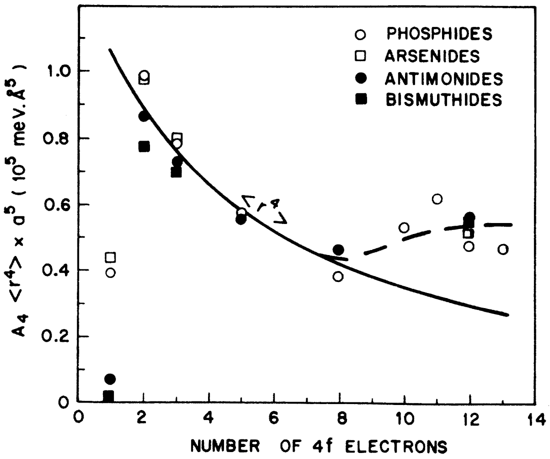

FIG. 1. Fourth-order crystal-field parameter times the lattice constant a raised to the fifth power in a number of rare-earth monopnictides. The solid line is the EPCM prediction with $Ze=-1.2$ and $\langle r^4\rangle$ equal to the Dirac-Slater values calculated by Lewis.

single 4f electron to the Fermi surface. We shall therefore exclude the Ce^{3+} compounds from further consideration. All the other pnictides, however, are found to follow a simple universal law when scaled by a^5. Thus this EPCM prediction seems to be confirmed in detail.

The dependence of $A_4\langle r^4\rangle a^5$ on the number of 4f electrons and hence $\langle r^4\rangle$ is, however, more complex. We show in Fig. 1 the variation of $\langle r^4\rangle$ across the rare-earth series. Using the relativistic absolute values for $\langle r^4\rangle$ calculated by Lewis[10] (see also Refs. 13 and 14), the solid line in Fig. 1 corresponds to an EPCM with $Ze = -1.2$. The agreement for all pnictides from PrX through TbX is clearly excellent. For elements beyond Tb, $A_4\langle r^4\rangle$ is found to increase somewhat, rather than continuing to decrease. For HoX to YbX, an effective charge of ~ -2 seems to be more appropriate. It is highly unlikely that there is a discontinuous change in the electronic properties at Ho and instead we believe that the increase in the effective charge at the heavy end simply represents a breakdown of the EPCM for $A_4\langle r^4\rangle$. It is difficult to identify the explicit mechanism responsible for this although an increased relative importance of covalency for the heavy rare earths seems to be the most likely candidate.

As noted above, $A_6\langle r^6\rangle$ is always small and indeed within the rather large relative errors it is approximately constant across the rare-earth series. The EPCM with $Ze = -2$ predicts that $A_6\langle r^6\rangle$ should vary from ~0.5 meV for PrP to ~0.15 meV for YbP. Thus again the EPCM gives approximately the right order of magnitude for the light rare earths, but it breaks down for the heavier atoms.

With the completion of this work there is now more information available on the crystal fields in the rare-earth pnictides than in any other isostructural series of compounds either insulating, semiconducting or metallic.[15] The significance of our results is perhaps best expressed as follows. It is now possible to deduce simply all of the low-lying electronic levels in any rare-earth pnictide, RX, for R from Pr to Yb and X from P to Bi given only the name of the compound and its lattice constant. $A_4\langle r^4\rangle$ may be obtained directly from Fig. 1 while one may take $A_6\langle r^6\rangle = 0.4 \pm 0.2$ meV for all compounds[16]; this scheme should give an over-all accuracy of 10–20%. Furthermore, for compounds with R from Pr to Tb, instead of Fig. 1, one may use the simple nearest-neighbor effective-point-charge model with $Ze = -1.2$. We hope, first, that these results will prove of empirical value in estimating crystal fields in both the pnictides and in other series of metallic compounds and, second, that the simple pattern we have established will help lead to a fundamental theory of crystal fields in metallic compounds.

Finally, we should emphasize that the effective point charge deduced here should not be interpreted too literally. For example, for Gd^{3+} the nonrelativistic Freeman-Watson calculations[9] give $\langle r^4\rangle = 1.515$ a.u.[4] while the Dirac-Slater calculations of Lewis[10] give $\langle r^4\rangle = 2.48$ a.u.[4] More recent fully relativistic Dirac-Fock calculations of Freeman and Desclaux[14] give $\langle r^4\rangle = 1.78$ a.u.[4] These correspond to effective charges of -1.9, -1.2, and -1.6, respectively. However, both the Hartree-Fock and Dirac-Slater methods give identical relative variations of $\langle r^4\rangle$ across the rare-earth series; thus the good agreement for the light rare earths evident in Fig. 1 does not seem to depend too sensitively on the calculational technique. Clearly both detailed form-factor measurements and Dirac-Fock calculations of $\langle r^4\rangle$ across the rare-earth series would be most useful in elucidating this point.

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[*] Guest scientist at Brookhaven National Laboratory, Upton, N.Y.

[†] Work at Brookhaven performed under the auspices of the U.S. Atomic Energy Commission.

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[15] For completeness we also include here results for CeBi and NdBi. From the neutron scattering spectra at 77 K, we find for CeBi: $|A_4\langle r^4\rangle \sim 0.15$ meV; for NdBi: $A_4\langle r^4\rangle = 6.33 \pm 0.2$ meV, $A_6\langle r^6\rangle = 0.53 \pm 0.1$ meV.

[16] H. L. Davis and H. A. Mook (unpublished) have recently reported CEF parameters for TmAs and TmBi which are in close agreement with those predicted using this scheme. For completeness we have included these in Fig. 1.