Field Gradient Induced by Organic Intercalation of Superconducting Layered Dichalcogenides

E. Ehrenfreund and A. C. Gossard

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

and

F. R. Gamble*

Syva Research Institute, 3221 *Porter Drive, Palo Alto, California*

Magnetic-resonance observations of niobium nuclei in both the layered dichalcogenide NbS_2 and the associated intercalation complex NbS_2 (pyridine)$_{1/2}$ yield different electric field gradients in the two compounds. At 4.2 °K, $e^2qQ/h = 60$ MHz in NbS_2 and 46 MHz in $NbS_2(Py)_{1/2}$. The difference is shown to arise from the conduction-electron term. It may result from charge transfer between the organic molecules and the conduction band of the layered dichalcogenide, or from redistribution of electrons between two overlapping conduction bands. The lattice sum for the field gradient is shown to be derived almost entirely from intralayer charges.

I. INTRODUCTION

Intercalation complexes of simple organic molecules and layered dichalcogenide metals have recently received much attention, especially because of their two-dimensional electrical-conductivity and superconducting properties.[1-4] The transition-metal–layered dichalcogenides are constructed from sandwiched layers in which a plane of metal atoms is surrounded by two planes of chalcogen atoms.[5] The bonding within the sandwiches is strong and primarily covalent; that between adjacent sandwiches is weak, primarily van der Waals's. In the intercalation complex the van der Waals's gap is opened and the organic molecules [pyridine (Py), for example] are inserted between adjacent sandwiches. Gamble *et al.*[4] have suggested that in the intercalation complexes of Lewis bases (electron donors) and layered sulfides the bonding between the molecules and the host sandwiches is not van der Waals's but rather involves some charge transfer from the intercalated molecule to the incompletely filled metallic bands. They have also suggested that in complexes involving pyridine and similar molecules, the molecular plane might be lying nearly parallel to the sandwich planes. These ideas were supported by x-ray and stoichiometry measurements and by the fact that group-Vb dichalcogenides, which are metallic, form these complexes while the group-VIb dichalcogenides, which possess one more valence electron per formula unit and are semiconductors, do not form them.

Charge transfer to the conduction band would alter the transition-metal Knight shift and electric field gradient (EFG). This effect is observed, indicating that the occupancy of the conduction band is indeed changed by intercalation.

II. EXPERIMENTAL

NbS_2 and the associated intercalation complex $NbS_2(Py)_{1/2}$ have been used in the present investigation. These materials have the layered structures described above, with the spacing between Nb planes being 6.27 Å in NbS_2 and 11.84 Å in $NbS_2(Py)_{1/2}$. The preparation of the samples is described elsewhere.[6] Both samples were superconductors at low temperatures; NbS_2 with superconducting transition temperature $T_C \approx 6$ °K and $NbS_2(Py)_{1/2}$ with $T_C \approx 4$ °K. Measurements have been performed on powdered samples using pulse NMR techniques as described earlier for $NbSe_2$.[7] The full quadrupolar structure was observed both in NbS_2 and $NbS_2(Py)_{1/2}$ and allows us to obtain the quadrupole-coupling constants, e^2qQ, and the Knight shift K for Nb^{93} in both materials. The measurements were performed in the temperature range 4–77 °K and at resonance frequencies around 50 MHz. Results for $|e^2qQ|$ and K are listed in Table I. It is seen that $|e^2qQ|$ is smaller by about 13 MHz in $NbS_2(Py)_{1/2}$ than in pure NbS_2. Using the value[8] $Q^{93} = -0.2$ b, a 13-MHz change in $|e^2qQ|$ is equivalent to $\Delta q = 1.9$ Å^{-3}. Also, $K_\perp$ (the shift for those nuclei with their symmetry axis perpendicular to the external magnetic field) is less negative (by $\sim 0.1\%$) in $NbS_2(Py)_{1/2}$ than in pure NbS_2. The measurements at 4.2 °K of both $K_\perp$ and $K_\parallel$[9] in NbS_2 show that the shift is anisotropic with $K_\parallel > K_\perp$. This is probably the case also for $NbS_2(Py)_{1/2}$ and for the measurements at higher temperatures, since in all cases the observed width of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is smaller than that expected by the second-order quadrupole interaction only.[10] The anisotropy of the Knight

TABLE I. Measured quadrupolar-coupling constants $|e^2qQ/h|$, and Knight shifts for Nb^{93} in NbS_2 and $NbS_2(Py)_{1/2}$. $|q|$ is obtained from $|e^2q/Qh|$ by assuming $Q^{93} = -0.2$ b (Ref. 8); the quoted error for Q^{93} in Ref. 8 is $\pm 50\%$. The accuracy of the measurements are ± 1 MHz in $|e^2qQ/h|$ and $\pm 0.08\%$ in the Knight shifts.

		NbS$_2$			NbS$_2$(Py)$_{1/2}$		
T (°K)		4.2	20	77	4.2	20	77
$|e^2qQ/h|$ (MHz)		60	60	59	46	45	47
$|q|$ (Å^{-3})		8.6	8.6	8.5	6.6	6.5	6.7
$K_\perp$ (%)		-0.2	-0.1	-0.1	$+0.02$	$+0.03$	$+0.01$
$K_\parallel$ (%)		$+0.3$					

shift indicates an anisotropic charge distribution around the niobium nuclei in both materials.

III. VARIOUS CONTRIBUTIONS TO ELECTRIC FIELD GRADIENT

It is convenient to divide the EFG at a Nb site into lattice and local components

$$eq = eq_{latt}(1 - \gamma_\infty) + eq_{loc}(1 - R) , \qquad (1)$$

where q_{latt} is the gradient due to all other charges, $\gamma_\infty \approx -15$ is the Sternheimer antishielding factor for Nb, q_{loc} is the contribution from the d electrons in the immediate vicinity of the niobium nuclei, and $R \approx 0.1$ is the corresponding shielding factor.[11]

The lattice part of NbS_2 is approximated by assuming point charges $+Ze$ (>0) for each Nb atom and $-\frac{1}{2}Ze$ for each S atom. Using the summation procedure of deWette for hexagonal lattices[12] we have computed the point-charge contribution for NbS_2 to be $q_{latt} = -0.250Z$ Å^{-3}. In order to obtain a picture of the role of the different layers in this lattice sum, we have evaluated this sum for several distances d between adjacent Nb planes (without changing the Nb-S distance within a layer). For all values of d greater than about 6 Å (in 2H-NbS$_2$, $d = \frac{1}{2}c = 6.27$ Å) we obtained for e^2qQ the same result as for NbS_2 (within 0.01%). We thus conclude that q_{latt} arises practically completely from intralayer charges, and the interlayer distance (provided it is greater than ~6 Å) does not affect q_{latt}.

The local part of the gradient is divided into a term q_v contributed by the valence electrons and a term q_c contributed by the conduction electrons. The Nb-S bonding can be regarded as mainly covalent. Since very little is known about the wave function of these valence electrons, we approximate their contribution to q_v in the following form[13]:

$$q_v = -\beta \langle r^{-3} \rangle_d n_d , \qquad (2)$$

where $\langle r^{-3} \rangle_d$ is averaged on the 4d Nb orbitals, $\beta = \langle 3\cos^2\theta - 1 \rangle$ is a geometric factor ranging between $+\frac{4}{7}$ and $-\frac{4}{7}$ taking into account the various d orbitals involved, and n_d is the effective number of the valence-band d electrons per atom. Schematically, the Nb contributes two d electrons and

two s electrons to form the compound NbS_2,[5] and thus $n_d \lesssim 2$. The most probable orbitals to form the covalent bond are those belonging to E'' (xz, yz orbitals) and E' (xy, $x^2 - y^2$ orbitals) representations,[5] and thus β is either $\beta(E'') = +\frac{2}{7}$ or $\beta(E')$ $= -\frac{4}{7}$. In the free ion, $\langle r^{-3} \rangle = 23$ Å^{-3} for[14] Nb^{+2}; in the compound, $\langle r^{-3} \rangle$ is somewhat smaller because of the expansion of the 4d orbitals in the solid.

NbS_2 has a single d electron outside the full valence bands. Semiempirical molecular-orbital calculations[5,15] suggest that in the transition-metal dichalcogenides with the trigonal prismatic structure the A_1 (or $3z^2-r^2$) orbitals (which have the smallest overlap with the ligand σ orbitals) form a narrow conduction band. Thus it seems reasonable to assume the contribution of these conduction electrons to the EFG is describable in a form similar to (2):

$$q_c = -\frac{4}{7} \langle r^{-3} \rangle n_{A_1} ,$$

where $\beta(A_1) = \frac{4}{7}$ and n_{A_1} is the number of electrons in the A_1 orbital. Substituting q_{latt}, q_v, and q_c into (1) and assuming, for instance, $\langle r^{-3} \rangle = 20$ Å^{-3}, $Z = 2$, $n_d = 2$, $n_{A_1} = 1$, we get for the total gradient, $q = -30$ Å^{-3} for $\beta = \frac{2}{7}$ and $q = +4$ Å^{-3} for $\beta = -\frac{4}{7}$. The experimental value is (Table I) $|q| = (9 \pm 5)$ Å^{-3}. Thus if this picture for the field gradient is a good approximation, it suggests that the valence d orbitals are primarily E' orbitals. However, since the sign of q was not determined in the experiment and the calculated q is a result of severe cancellation, reaching any definite conclusion is hazardous.

Insertion of pyridine between the layers of NbS_2 increases the distance d between Nb planes from 6.27 to ~12 Å and increases the basal-plane lattice parameter a by $\frac{1}{3}\%$.[6] In addition, free pyridine has an electric dipole moment p (of ~2.1 D)[16] lying in the plane of the ring. The EFG induced by an electric dipole moment can be derived directly from the expression for its electric field; its zz component is given by

$$V_{zz} = \left(1 - \frac{5z^2}{r^2}\right) \frac{3\vec{r} \cdot \vec{p}}{r^5} + \frac{6zp_z}{r^5} . \qquad (3)$$

The exact positions of the pyridine molecules are at present not known and thus the lattice sum for calculating the EFG cannot be evaluated. However, it has been suggested[4] that these molecules are lying with their planes parallel or nearly parallel to the chalcogenide layers. Furthermore, since the lattice sum for the EFG produced by permanent dipoles converges much faster (r^{-4}) than that produced by point charges (r^{-3}), it seems that taking into account the first shells of nearest neighbors should yield the right order of magnitude for the permanent dipoles EFG. We have chosen ar-

bitrarily a symmetry with six pyridine molecules lying in the first shells of neighbors and found that the associated q is of the order of 0.01 Å^{-3} for $p = 2$ D and a distance of 4 Å between the niobium plane and the pyridine's plane of stacking. This number is much smaller than each of the other terms calculated above and therefore we shall ignore it in the following.

IV. DISCUSSION

The above consideration of the EFG shows that the lattice contributions are practically the same in both NbS_2 and $NbS_2(Py)_{1/2}$. The valence-electron contributions should also remain the same because of the unchanged point symmetry of the niobium atoms and the almost unaltered nearest-neighbor distance.[6] Thus it is quite reasonable to assume the experimental change Δq in the EFG to arise from a change Δn in the number of the conduction d electrons per niobium atom. The observed $\Delta q = (2 \pm 1)$ Å^{-3} is equivalent to $\Delta n = 0.16 \pm 0.08$ for the A_1 electrons in the conduction band. This change in the occupation of the conduction band may arise in two ways. First there may be direct charge transfer between the pyridine and the NbS_2 d band in the process of intercalation. Alternatively, the change in d-band occupation could result from a shift in the position of an overlapping s-p band upon intercalation. Based on Hall and Seebeck data, it was suggested[15] that in NbS_2, for instance, there is an overlap between the narrow d conduction band and a nearly filled broad valence band consisting mainly of s and p orbitals of the anion. Bonding with the pyridine would lower the broad valence band, transferring electrons into the narrow d conduction band.[17] Previous measurements[4] indicated that the interaction responsible for the intercalation involves some donation of the lone-pair nitrogen electrons to the partially filled conduction band of the metallic dichalcogenide.

An increase in the number of the electrons in the A_1 orbital would add a negative contribution to the total q, and thus increase $|q|$ if q is negative or rather decrease $|q|$ if q is positive. Experimentally $|q|$ decreases by intercalation, thus the above picture suggests a positive q and as stated before, the possibility of positive q indicates E' orbitals to be the primary valence d orbitals. A net increase in the conduction electrons would reduce Z in the same amount and accordingly reduce

$|q_{latt}|$. Taking into account this effect too, we finally find $\Delta n = 0.2 \pm 0.1$ for the increase in the number of conduction electrons per niobium atom by intercalating NbS_2 with pyridine.

The observed difference in $K_\perp$ of Nb^{93} nuclei in the two compounds supports too a picture of a different number of d electrons per atom. However, because of the large anisotropy of the shift, the unknown relative contribution of the s- and d-band terms, and the unknown structure of the density-of-states curve, based on the Knight-shift results alone, it is very difficult to make a quantitative estimate of the change in the d-band occupation.

V. CONCLUSION

Effects of the bonding of intercalated organic layers with layered metallic compounds have been observed using NMR. The relatively stronger bonding between organic and host layers, which one expects in comparison with the layer-layer host interactions, produces readily observable effects on the metal-atom NMR. In the particular NbS_2-pyridine system studied here, a field gradient change at the nucleus exceeding 20% occurred upon intercalation. A consideration of the purely structural contributions to the field gradient change implied that the changes in interatomic distances upon intercalation are entirely too small to produce the observed effects. Changes in the structure and occupation of the conduction bands are required with the redistribution of approximately 0.2 d-band electrons per niobium atom in the present case. Such a redistribution is perhaps necessary in order to achieve a bond between organic and metal layers strong enough to permit interweaving of the metallic sandwich layers with organic layers. It might be hoped that similar, *in situ*, studies on the organic sites will reveal more information on the bonding and might also give some insight into the role of the organic molecules in the conductivity and superconductivity processes.

*Present address: Corporate Research Laboratory, Esso Research and Engineering Co., P.O.B. 45, Linden, N.J.

[1]F. R. Gamble, F. J. DiSalvo, R. A. Klemm, and T. H. Geballe, Science 168, 568 (1970).

[2]T. H. Geballe, A. Menth, F. J. DiSalvo, and F. R. Gamble, Phys. Rev. Letters 27, 314 (1971).

[3]F. J. DiSalvo, R. Schwall, T. H. Geballe, F. R. Gamble, and J. H. Osiecki, Phys. Rev. Letters 27, 310 (1971).

[4]F. R. Gamble, J. H. Osiecki, and F. J. DiSalvo, J. Chem. Phys. 55, 3525 (1971).

[5]See, for example, J. A. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

[6]F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, Science **174**, 493 (1971).

[7]E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geballe, J. Appl. Phys. **42**, 1491 (1971).

[8]K. Murakawa, Phys. Rev. **98**, 1285 (1955).

[9]The powder particles are typically in the form of flakes. Depending on particle size and packing and the manner in which the sample was cooled, substantial orientation of the flakes was sometimes achieved, with the c axis parallel to the external magnetic field. In these cases we could also measure $K_\parallel$. This was achieved in the NbS_2 sample but not in our $NbS_2(Py)_{1/2}$ sample, probably because of shape differences.

[10]W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, Phys. Rev. **132**, 1898 (1963).

[11]In the absence of (anti-) shielding calculations for Nb, use was made of Murakawa's (Ref. 8) and Burns's [G. Burns, J. Chem. Phys. **31**, 1253 (1959)] estimates for R and γ_∞, respectively.

[12]F. W. DeWette, Phys. Rev. **123**, 103 (1961).

[13]See, for example, M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 360.

[14]A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA, p. 291.

[15]R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, J. Solid State Chem. **3**, 56 (1971).

[16]L. G. Wesson, *Tables of Electric Dipole Moments* (MIT Press, Cambridge, Mass., 1949), p. 23.

[17]A qualitatively similar situation occurs in transition-metal hydrides. Bonding between hydrogen levels and conduction-band states induces bonding states far below the Fermi energy. [S. Alexander (private communication); see also, D. E. Eastman, J. K. Cashion, and A. C. Switendick, Phys. Rev. Letters **27**, 35 (1971); and E. Ehrenfreund, Ph.D. thesis (The Hebrew University, Jerusalem, Israel, 1970) (unpublished).]

Electron-Spin Resonance of Rare-Earth Ions in the Actinide Cubic Metal Th[†]

D. Davidov, R. Orbach, C. Rettori,[*] D. Shaltiel,[‡] and L. J. Tao

Department of Physics, University of California, Los Angeles, California 90024

and

B. Ricks[§]

Department of Physics, University of California, San Diego, California 92037

(Received 25 August 1971)

The electron-spin resonance of Gd, Er, and Dy of nominal concentrations between 40 and 3250 ppm in the actinide metal Th is reported. The temperature dependence of the linewidth yields values for the exchange coupling J_{fs} between the rare-earth localized moment and the conduction electrons. We find J_{fs} to be almost independent of the $4f$ occupation number, in agreement with the values of J_{fs} obtained previously by others from superconducting-transition-temperature measurements in the same alloys.

I. INTRODUCTION

We wish to report the observation of the electron-spin resonance (ESR) of the rare earths Er, Dy, and Gd in the cubic actinide metal thorium (the observation of Er in Th has been reported previously).[1] The temperature dependence of the linewidth, as well as the sign of the g shift, yield values for the localized-moment–conduction-electrons exchange coupling J_{fs}. We find that J_{fs} is positive, and almost equal for the three solutes. This behavior can be understood using the usual model of a total exchange interaction generated from a positive atomic-like contribution expected to be nearly independent of the $4f$ occupation number, and a (negative) covalent mixing contribution which does vary across the rare-earth series, but which is expected to be small in comparison to the atomiclike term.[2] The values of J_{fs} so derived are in agreement with the

values of J_{fs} obtained by fitting the Abrikosov-Gorkov model[3] with the experimental decrease of the superconducting transition temperature T_c of Th when alloying with the same rare earths, as measured by Guertin.[4]

II. SAMPLE PREPARATION

The ESR measurements were conducted at 3-cm wavelength and as a function of temperature in the liquid-helium range ($1.4 \le T \le 4.2$ °K). The apparatus and technique of measurement are described elsewhere.[5]

The samples were arc melted from thorium of 99.99% purity and rare earths of minimum 99.9% purity in an argon atmosphere. After melting, the samples were prepared by two different methods:

(i) *Rapid quenching.* The rapid quenching was accomplished by splattering the molten alloys on a cold copper wall with a jet of He gas. The "splat-