

show that (a) the phonon-induced structure in N_S is enhanced in the Pb(+) bias and suppressed in the Pb(-) bias, and (b) this enhancement and suppression effect increases with decreasing electron concentration of the Si electrodes, i. e., with increasing asymmetry in the normal conductance.

In normal metal-oxide-superconductor junctions, the normal conductance seldom varies by more than 5% over the phonon energy range of the superconductor. The asymmetry effect discussed here is, therefore, negligible and $(dI/dV)_S/(dI/dV)_N$

measures N_S directly. In contrast, the normal-conductance asymmetry observed in Si-Pb junctions is common to most degenerate semiconductor-superconductor contacts. Since the asymmetry can be controlled by properly choosing the carrier concentration of the semiconductor electrode, it should be possible to utilize this enhancement effect to study the fine structure in N_S of the more weakly coupled superconductors, e. g., Al and Zn, which has not been possible with metal-oxide-metal junctions.

¹D. C. Tsui, Phys. Rev. Letters **27**, 574 (1971).

²J. R. Schrieffer, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum, New York, 1969), Chap. 21.

³W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 11, and private communication.

Electron Spin Resonance of Mn^{2+} in BaF_2 , SrF_2 , CdF_2 , and CaF_2 [†]

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Electron-spin-resonance investigations of the Mn^{2+} center in BaF_2 , CdF_2 , and SrF_2 are reported and spin-Hamiltonian parameters are given. Previously reported values for the Mn^{2+} center in CaF_2 are given for comparison.

We have recently reported¹ a critical analysis of the ESR spectra obtained from the Mn^{2+} center present in dilute concentrations in CaF_2 . As a result, several uncertainties associated with earlier investigations have been resolved and accurate values for the spin-Hamiltonian constants of this system have been determined. This addendum reports the results of our subsequent ESR investigations of the Mn^{2+} center in the isomorphous hosts BaF_2 , SrF_2 , and CdF_2 . Single-crystalline samples of BaF_2 , SrF_2 , and CdF_2 were obtained from Optovac, Inc. The ESR data obtained from the

samples of SrF_2 and CdF_2 , both containing nominally 10^{-3} wt% Mn^{2+} , exhibited fluorine superhyperfine structure similar in resolution and appearance to that observed in the CaF_2 system. These data were analyzed in a manner closely following that employed for CaF_2 , which was described in detail in Ref. 1. The best-fitted spin-Hamiltonian parameters to the experimental data are shown in Table I, in which we include the results of CaF_2 for comparison.

The ESR spectra observed in the BaF_2 crystal with a 10^{-3} -wt%- Mn^{2+} concentration also displayed

TABLE I. Room-temperature spin-Hamiltonian parameters, lattice constants (r), observing ESR microwave frequencies (f), and linewidths (ΔH) for Mn^{2+} in CaF_2 , BaF_2 , SrF_2 , and CdF_2 .

Host	CaF_2	BaF_2	SrF_2	CdF_2
A (G)	-100.8 ± 0.1	-97.7 ± 0.1	-100.9 ± 0.1	-100.1 ± 0.1
g	2.0010 ± 0.0005	2.0013 ± 0.0005	2.0010 ± 0.0005	2.0012 ± 0.0005
$T_{ }$ (G)	15.3 ± 0.1	11.9 ± 0.5	13.1 ± 0.1	15.65 ± 0.1
T_{\perp} (G)	6.3 ± 0.1	5.4 ± 0.5	5.35 ± 0.1	6.6 ± 0.1
a (G)	0 ± 0.1	0 ± 0.5	0 ± 0.1	0.2 ± 0.1
ΔH (G)	2.1 ± 0.1	5-7	2.1 ± 0.1	2.1 ± 0.1
f (GHz)	9.51192 ± 0.00005	9.50951 ± 0.00005	9.50660 ± 0.00005	9.41580 ± 0.00005
r (Å) ^a	5.46295	6.2001	5.7996	5.3880

^aR. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963), Vol. I, p. 241.

resolved fluorine superhyperfine structure, but the resolution of this structure was noticeably poorer than that observed for the other fluorite crystals. In an attempt to observe the superhyperfine structure with improved resolution, we investigated a series of BaF₂ crystals with lower Mn²⁺ concentrations. However, the ESR spectra from these crystals did not display any better resolution. This fact is reflected in Table I by the relatively large error limits for the BaF₂ system.

We have also found that the linewidths of the best-fitted theoretical spectra for BaF₂ varied with crystal orientation, i. e., the linewidths for the [100], [110], and [111] spectra were found to be 7, 5, and 6 G, respectively. As shown in Table I, the other systems all have a best-fitted line-

width of 2.1 G, independent of the crystal orientation.

This behavior of the BaF₂ data can be explained if it is assumed that the Mn²⁺ ions tend to cluster in the BaF₂ lattice, which has a larger lattice parameter than the other fluorite lattices. The major contribution to the observed linewidth would then be due to the dipole-dipole interaction between Mn²⁺ ions in this cluster. As a test of this hypothesis, we calculated the second moment for the Mn²⁺ ESR line assuming all the nearby Ba²⁺ sites were occupied by Mn²⁺ ions up to the tenth shell. The resultant second moment displayed an angular variation which is consistent with the trend exhibited by the measured best-fitted linewidth for the three crystallographic directions.

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†R. J. Richardson, Sook Lee, and T. J. Menne, Phys. Rev. B 4, 3837 (1971).

Differences in the Temperature Dependence of the Hyperfine Field and Magnetization of Ferromagnetic Metals

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The temperature dependences of the magnetization and of the hyperfine field in ferromagnetic metals such as Fe or Ni are different even after transformation to constant volume. It is suggested that the effect of lattice vibrations can explain the observed explicit temperature dependence of the hyperfine field at constant volume and that the deviation of the latter from the temperature dependence of the magnetization at constant pressure is well described by considering the thermal expansion also. Some applications of this model to related problems are discussed.

In a pure ferromagnetic metal at constant pressure, the temperature dependence of the hyperfine field is not precisely the same as that of the spontaneous magnetization. The first observation of this effect was the nuclear-magnetic-resonance (NMR) measurement of Robert and Winter¹ in iron. The agreement between the temperature dependence of the hyperfine field measured by NMR and the Mössbauer effect (ME) indicates² that the deviation of the hyperfine field and bulk magnetization with increasing temperature is not connected with the domain structure of the metal, because the NMR measurements are associated with nuclei within the domain walls, while the ME measurements involve chiefly nuclei within the domains themselves.

When the temperature dependence of the reduced hyperfine field h is compared with the reduced magnetization σ , transforming both to constant volume

to eliminate any differential effects of thermal expansion, it is found^{2,3} that even at constant volume there still remains an explicit temperature dependence of the hyperfine coupling constant A , i. e.,

$$h(T) = A(T)\sigma(T). \quad (1)$$

The explicit temperature dependence of A for pure iron between 0 and 300 °K can be fitted within experimental accuracy to

$$A(T) = 1 - aT^2, \quad (2)$$

where $a = 0.77 \times 10^{-7} \text{ }^\circ\text{K}^{-2}$ (Ref. 3) or $0.4 \times 10^{-7} \text{ }^\circ\text{K}^{-2}$ (Ref. 2) is obtained, depending on the magnetization data used.

The situation is similar⁴ for Ni, except that at constant pressure the deviation between the temperature dependence of the relative hyperfine field and the relative magnetization is approximately