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Susceptibility and Entropy of F-Centers in Alkali Halides below 1°K*

J. Korringa and J. G. Daunt
Department of Physics and Astronomy, Ohio State University, Columbus, Ohio

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The entropy and the paramagnetic susceptibility of F-centers in alkali halides below 1°K for alkali nuclei with spin $\frac{3}{2}$ have been computed using the model of Kip *et al.* in which the predominant perturbation of the electron in the F-center is the magnetic interaction with the neighbor alkali nuclei. The lower limits of temperature possible by magnetic cooling of such systems are set forth and considerations are given as to the practical possibility of such cooling of F-center assemblies.

1. INTRODUCTION

The experiments of Heer and Rauch[1] showed that the paramagnetic susceptibility of F-centers in additively colored KCl obeyed Curie's law down to 1°K. In view of the fact that F-centers present a system the number density of which can be readily varied or selected in the range 10^{19} centers/cm^3 and lower, it was considered that they might present an interesting substance for magnetic cooling in that the dipole-dipole interactions could be made arbitrarily small. We have calculated therefore some of the properties at very low temperatures of F-centers in alkali halides, e.g., the entropy and susceptibility, and have used the model proposed by Kip *et al.*[2] in which the predominant perturbation for the electron in the F-center is the magnetic interaction with the six neighboring alkali nuclei. It is shown that this hyperfine interaction imposes the lowest limit on the final temperatures possibly obtainable by adiabatic demagnetization of F-centers in alkali halides, and numerical evaluations are given for these limits. In making the computations we have limited ourselves to alkali nuclei with spin $\frac{3}{2}$ which is the value of I for the majority, and we have neglected for preliminary simplicity other hyperfine interactions, such as for example magnetic interaction of the F-center with neighboring halide nuclei and quadrupole interactions, which clearly must play some role, particularly for alkali halides containing Br or I.

It is concluded that measurements of the thermal and paramagnetic properties below 1°K of these systems would provide an additional method of assessing the validity of the theoretical model, complementary to the microwave magnetic resonance method already employed.

2. COMPUTATION OF THE ENTROPY AND SUSCEPTIBILITY

Following the suggestion of Kip *et al.*,[2] the Hamiltonian for the system consisting of an F-center electron and its six nearest neighboring alkali nuclei in an external magnetic field H along the z-axis will be written as

$$\mathcal{H}=\tfrac{1}{6}\xi' A\mathbf{S}\cdot\mathbf{I}-\tfrac{1}{2}g\mu_0 HS_z. \tag{1}$$

Here $\mathbf{I}=\sum\mathbf{I}_i$ is the sum of the angular momenta of the six alkali nuclei in units of $\hbar/2$, $\mathbf{S}$ is the angular momentum of the electron in the same units, A is the constant of hyperfine structure coupling of a free alkali atom and $\frac{1}{6}\xi'$ is the ratio of the probability density of the electron in an F-center to that of the valency electron in the free atom at an alkali nucleus; ξ' is of the order of magnitude unity, as has been shown by Kip *et al.* g and μ_0 are the electronic splitting factor and Bohr magneton, respectively.

In terms of the sum over states, Z,

$$Z=\textstyle\sum_n \exp(-E_n/kT), \tag{2}$$

the entropy S and the susceptibility χ are given by

$$S(T,H)/k=\ln Z+T\partial\ln Z/\partial T, \tag{3}$$

$$\chi(T)=kT(\partial^2\ln Z/\partial H^2)_{H=0}. \tag{4}$$

The coupling constant for the interaction between electron and the nuclei will be eliminated by defining a reduced temperature, T^*, and a reduced magnetic field, H^*, as

$$T^*=T/T_c,\quad H^*=g\mu_0 H/2kT_c, \tag{5a}$$

where the coupling is characterized by a temperature T_c and an energy E_c defined by

$$E_c=kT_c=\xi' A/3. \tag{5b}$$

Furthermore, we will write:

$$\gamma=H^*/T^*=g\mu_0 H/2kT.$$

In the calculation of $S(T,H=0)$ the second term in (1) is absent and in the calculation of $\chi(T)$ it may be treated as a small perturbation of which only contributions up to the second order are of interest. The first term of (1) represents the cosine coupling between two vectors. Its eigenfunctions and eigenvalues can be expressed in terms of the nuclear states with well defined values of $(\mathbf{I}\cdot\mathbf{I})$ and I_z. Restricting ourselves to nuclei with spin $\frac{3}{2}$ (i.e., Li^7, Na^{23}, K^{39}, K^{41}, Rb^{87}), the eigenvalues of these operators are $\hbar^2K(K+1)$ and $\hbar M(M=K, K-1,\cdots -K)$, respectively, where K takes the values 9, 8, $7\cdots 1$, 0. Let the corresponding states

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[1] C. V. Heer and C. Rauch, Phys. Rev. **90**, 530 (1953).

[2] Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).

be $\varphi_{K,r}{}^{M}$; r lables the mutually orthogonal sets with the same K which exist owing to permutations of the nuclei. The number $g(K)$ of such sets for a given K is:

$K=$	9	8	7	6	5	4	3	2	1	0
$g(K)=$	1	5	15	35	64	96	120	120	90	34

The normalized eigenfunctions of (1) for $H=0$, in which the electronic and resulting nuclear spins are parallel and antiparallel, respectively, are as follows:

$$\Phi_{K+\frac{1}{2},\,r}{}^{M+\frac{1}{2}}=\left(\frac{K+M+1}{2K+1}\right)^{\frac{1}{2}}\varphi_{K,\,r}{}^{M}\xi+\left(\frac{K-M}{2K+1}\right)^{\frac{1}{2}}\varphi_{K,\,r}{}^{M+1}\eta,$$

$$\text{eigenvalue } E_{K,+}{}^{0}=KE_c, \tag{6a}$$

$$\Phi_{K-\frac{1}{2},\,r}{}^{M+\frac{1}{2}}=\left(\frac{K-M}{2K+1}\right)^{\frac{1}{2}}\varphi_{K,\,r}{}^{M}\xi-\left(\frac{K+M+1}{2K+1}\right)^{\frac{1}{2}}\varphi_{K,\,r}{}^{M+1}\eta,$$

$$\text{eigenvalue } E_{K,-}{}^{0}=-(K+1)E_c. \tag{6b}$$

The nonvanishing matrix elements of the perturbation by the magnetic field are, for any values of r,

$$\begin{aligned}(-E_cH^*S_z)_{K\pm\frac{1}{2},\,K\pm\frac{1}{2}}{}^{M+\frac{1}{2},\,M+\frac{1}{2}}&=\mp\frac{2M+1}{2K+1}E_cH^*,\\ (-E_cH^*S_z)_{K+\frac{1}{2},\,K-\frac{1}{2}}{}^{M+\frac{1}{2},\,M+\frac{1}{2}}&=-\frac{2[(K+M+1)(K-M)]^{\frac{1}{2}}}{2K+1}E_cH^*.\end{aligned} \tag{7}$$

The first- and second-order perturbations of the energy are, therefore,

$$\begin{aligned}E_{K,\,M,\,\pm}{}^{(1)}&=\mp E_cH^*\frac{2M+1}{2K+1},\\ E_{K,\,M,\,\pm}{}^{(2)}&=\pm E_cH^*\frac{4}{(2K+1)^3}(K+M+1)(K-M).\end{aligned} \tag{8}$$

With these results, valid for $H^*\ll 1$, the sum over states takes the form,

$$\begin{aligned}Z(T^*,H^*)=&\sum_{K=0}^{9}g(K)\exp\left(\frac{-K}{T^*}\right)\sum_{M=-K-1}^{K}\exp\left\{\frac{2M+1}{2K+1}\gamma-\frac{4}{(2K+1)^3}(K+M+1)(K-M)\gamma^2T^*\right\}\\ &+\sum_{K=1}^{9}g(K)\exp\left(\frac{(K+1)}{T^*}\right)\sum_{M=-K}^{K-1}\exp\left\{-\frac{2M+1}{2K+1}\gamma+\frac{4}{(2K+1)^3}(K+M+1)(K-M)\gamma^2T^*\right\}.\end{aligned} \tag{9}$$

For $H^*=0$ we obtain

$$Z(T^*,0)=2g(0)+2\exp\left(\frac{1}{2T^*}\right)\sum_{K=1}^{9}g(K)\times\left[(2K+1)\cosh\left(\frac{2K+1}{2T^*}\right)-\sinh\left(\frac{2K+1}{2T^*}\right)\right], \tag{10}$$

from which the entropy can be calculated. The susceptibility is

$$\begin{aligned}\chi(T^*)=\frac{(\frac{1}{2}g\mu_0)^2}{kT_cT^*}\frac{1}{Z(T^*,0)}\Bigg[&2g(0)+\frac{2}{3}\sum_{K=1}^{9}\frac{g(K)}{2K+1}\times\left\{(K+1)(2K+3)\exp\left(\frac{-K}{T^*}\right)+K(2K-1)\exp\left(\frac{(K+1)}{T^*}\right)\right\}\\ &+\frac{16}{3}T^*\sum_{K=1}^{9}g(K)\frac{K(K+1)}{(2K+1)^2}\times\left\{\exp\left(\frac{(K+1)}{T^*}\right)-\exp\left(\frac{-K}{T^*}\right)\right\}\Bigg].\end{aligned} \tag{11}$$

Numerical evaluations of the entropy and the susceptibility as a function of T^* are given in Table I and Figs. 1 and 2.

It will be seen in Fig. 1 that the entropy, S, per unit F center asymptotically approaches $13k\ln 2$ for $T\gg T_c$. This is because each of the six alkali ions surrounding the F center has spin entropy of $k\ln(2I+1)$ for completely disordered spins and, having assumed above that $I=\frac{3}{2}$ throughout, we get for all ions an amount $6\times k\ln 4=12k\ln 2$. The remaining $k\ln 2$ gives the electron contribution.

It will also be noted, as would be expected, that S begins to decrease markedly from the value $13k\ln 2$

TABLE I. Numerical values of the entropy $S(T^*,0)/k$ and the susceptibility χ^* as a function of the reduced temperature T^* for the F-center model as computed from Eqs. (3), (10), and (11).

T^*	$S(T^*,0)/k$	$\chi^*\equiv\chi(T^*)\cdot\left(\frac{4kT_c}{g^2\mu_0{}^2}\right)$
0.10	2.89	3.06
0.20	3.07	1.56
0.33	3.81	0.97
0.50	4.86	0.67
0.67	5.72	0.53
1.00	6.79	0.39
1.67	7.65	0.29
2.00	7.86	0.27
2.50	8.08	0.24
3.33	8.34	0.21
5.00	8.63	0.17
10.00	8.90	0.10
20.00	8.98	0.05
100.00	9.01	0.01

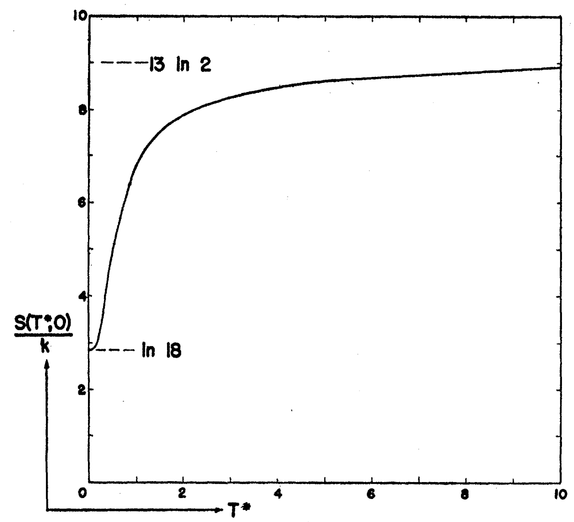

Fig. 1. The entropy $S(T^*,0)/k$ per F-center as a function of the reduced temperature T^*. The maximum value is 13 ln2, the minimum ln18. The latter value corresponds to a total spin $=8\frac{1}{2}$ ($\frac{3}{2}\times 6$ for the six nearest neighbor alkali nuclei $-\frac{1}{2}$ for the electronic spin).

when T becomes approximately equal to T_c. It must be clearly remembered that this entropy computation reflects only the effect of the magnetic hyperfine interaction between the F-center and its nearest neighboring alkali nuclei (provided only that these have $I=\frac{3}{2}$). No attempt has been made in this preliminary work to take account of other hyperfine interactions, which can occur, namely (a) the coupling between the F-center and the nearest neighboring halide nuclei, (b) the coupling between the F-center and next nearest neighbor alkali nuclei and (c) quadrupole interactions. The experiments of Kip *et al.*[2] on the paramagnetic resonance of F-centers in KCl crystals indicate that (a) and (b) are relatively small for this substance. For other alkali halides with Br and I the interactions (a) may become of considerable importance relative to that between F-center and its surrounding alkali nuclei; and it would be expected that, because of the large quadrupole moments in Br and I, interaction (c) would also be significant. Kip *et al.* had already made significant progress in the experimental evaluation of interaction (a) from their F-center magnetic resonance measurements.

3. APPROXIMATIONS FOR S, $\chi(T)$, AND C_v

Approximate expressions for the entropy S, the susceptibility $\chi(T)$, and the magnetic specific heat C_v, valid for $T^*\gg 1$ can be obtained by power series expansion. We find

$$Z(T^*,0)=2^{13}\left[1+\frac{a}{2T^{*2}}+\frac{a}{6T^{*3}}+\cdots\right] \tag{12}$$

and

$$\chi(T^*)=\frac{(\frac{1}{2}g\mu_0)^2}{kT_cT^*}\left[1-\frac{2a}{9T^{*2}}-\frac{a}{9T^{*3}}+\cdots\right], \tag{13}$$

where

$$a=\sum g(K)K(K+1)(2K+1)/\sum g(K)(2K+1)=45/2.$$

Therefore, for $T^*\gg 1$,

$$S(T^*,0)/k=13\ln 2-\frac{45}{4}\left[\frac{1}{T^{*2}}+\frac{2}{3T^{*3}}+\cdots\right], \tag{14}$$

$$\chi(T^*)=\frac{(\frac{1}{2}g\mu_0)^2}{kT_cT^*}\left[1-\frac{5}{T^{*2}}-\frac{5}{2T^{*3}}+\cdots\right]\text{emu/cm}^3, \tag{15}$$

$$C_v/k=\frac{45}{2}\left[\frac{1}{T^{*2}}+\frac{1}{T^{*3}}\cdots\right], \tag{16}$$

where the quantities are all per unit F-center.

Unfortunately the foregoing series are not very rapidly convergent. The use of Eq. (16) is therefore limited to values of T^* greater then about 10.

For $T^*\leqslant 0.5$, $\chi(T^*)$ can be written with less than 1% error as

$$\chi(T^*)=\frac{(\frac{1}{2}g\mu_0)^2}{kT_c}\frac{17}{57}\left(\frac{1}{T^*}+0.247\right). \tag{17}$$

4. PROPERTIES OF F-CENTERS FOR MAGNETIC COOLING

The maximum number of F-centers that can be conveniently produced in alkali-halides by additive coloration[3] is about 10^{19} per cm^3. Splitting of the magnetic sublevels due to dipole-dipole interaction between the F-centers themselves would be expected to

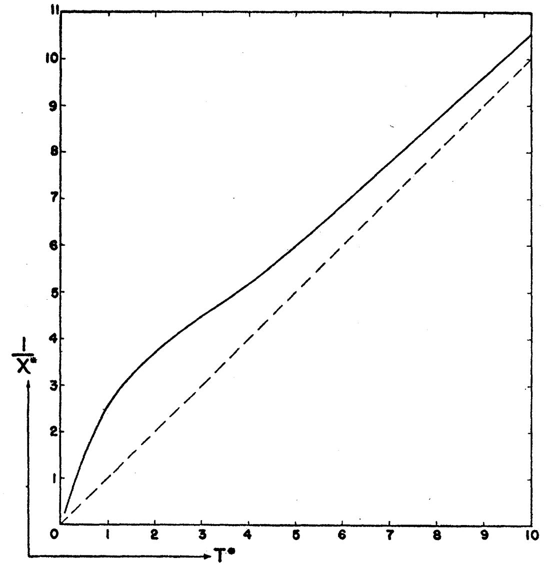

Fig. 2. The reciprocal of the reduced electronic paramagnetic susceptibility $1/\chi^*=[1/\chi(T^*)](g^2\mu_0{}^2/4kT_c)$ as a function of the reduced temperature, T^*. The broken curve gives the Curie law valid for high temperatures, namely $\chi(T^*)=(g^2\mu_0{}^2)/(4kT_cT^*)$.

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[3] F. Seitz, Revs. Modern Phys. **18**, 384 (1946); **26**, 7 (1954).

occur at temperatures T_{dip} equal to or less than $g^2\mu_0^2/kr^3 \approx 3\times10^{-5}$°K where r is the average distance between F-centers. Such temperatures, T_{dip} are much lower than those (T_c) characterizing the hyperfine energy as can be seen in Table II. Table II specifies the known values of the nuclear spins, magnetic moments, and quadrupole moments of the alkali and halide nuclei together with the observed hfs coupling constant A for the *free* atom. The values of T_c/ξ' characterizing the hyperfine structure for F-centers due to coupling with the nearest neighbor alkali nuclei, as defined by Eq. (5b), are computed from the free-atom values of A.

The lowest temperatures, therefore, which could be reached by magnetic cooling techniques using F-centers as the paramagnetic working substance would be determined by the hyperfine coupling rather than dipole-dipole interaction. If the major hyperfine coupling is the magnetic interaction with the nearest neighbor alkali nuclei, then the entropy determinations of Sec. 2 above may be used to estimate the lowest temperatures available by magnetic cooling, as follows: first the entropy changes that can be produced during the initial high temperature isothermal magnetizations in strong magnetic fields ($T^*\gg1$, $H^*\gg1$) can be calculated by considering the first term in (1) as a perturbation on the second term. The eigenfunctions of $-\frac{1}{2}g\mu_0HS_z$ which have at the same time a well-defined value of $(\mathbf{I}\cdot\mathbf{I})$ and I_z are

$$\Psi_{K,+,r}{}^M=\varphi_{K,r}{}^M\xi,\quad \Psi_{K,-,r}{}^M=\varphi_{K,r}{}^M\eta. \tag{18}$$

TABLE II. Pertinent data for nuclei of alkali-halides with evaluation of the characteristic hyperfine coupling temperature, T_c, in terms of the parameter ξ'.[a]

Atom	I	Natural abundance (percent)	μ nuclear magnetons	Q ($1\theta^{-24}$ cm^2)	A cm^{-1}	T_c/ξ' millidegrees absolute
Li^6	1	7.52	+0.822	0.0005	0.0038	2.04
Li^7	3/2	92.47	+3.25	(0.02)	0.0133	6.36
Na^{23}	3/2	100	+2.22		0.0296	14.16
K^{39}	3/2	93.08	+0.391		0.0077	3.68
K^{40}	4	0.012	−1.29		0.0214	10.24
K^{41}	3/2	6.91	+0.215		0.0042	2.00
Rb^{85}	5/2	72.15	+1.35		0.0506	24.72
Rb^{87}	3/2	27.85	+2.75		0.114	54.8
Cs^{133}	7/2	100	+2.58	$\leqslant 0.3$	0.153	73.2
F^{19}	1/2	100	+2.63			
Cl^{35}	3/2	75.4	+0.822	−0.079		
Cl^{37}	3/2	24.6	+0.684	−0.062		
Br^{79}	3/2	50.52	+2.11	+0.26		
Br^{81}	3/2	49.48	+2.27	+0.21		
I^{127}	5/2	100	+2.81	−0.59		

[a] Data for this table have been taken from: *Experimental Nuclear Physics*, edited by E. Segrè (John Wiley and Sons, New York, 1953), Vol. 1, p. 434 (part by N. F. Ramsey) and p. 682 (part by K. T. Bainbridge); also from J. B. M. Kellogg and S. Millman, Revs. Modern Phys. **18**, 323 (1946).

The energy of the second order in the perturbation is

$$\frac{1}{E_c}E_{K,\pm}{}^M=\mp H^*\pm M\mp(1\pm M)(K\mp M+1)/2H^*. \tag{19}$$

Inserting this into (2) and expanding for $T^*\gg1$, we obtain

$$Z(T^*,\gamma)=2^{13}\left[\left(1+\frac{15}{4T^{*2}}+\cdots\right)\cosh\gamma + \left(\frac{15}{2\gamma T^{*2}}+\cdots\right)\sinh\gamma\right], \tag{20}$$

and from this we get

$$S(T^*,\gamma)/k=13\ln2+\ln\cosh\gamma-\gamma\tanh\gamma - \frac{15}{4T^{*2}}(1+2/\cosh^2\gamma)+\cdots, \tag{21}$$

where the second and third terms on the righ-hand side represent the usual Brillouin function for the electronic entropy for spin $\frac{1}{2}$ and the fourth term shows the effect of the hyperfine structure.

Now if the initial temperature T_i of isothermal magnetization be taken as 1°K, terms in $1/T^{*2}$ in Eq. (21) can be neglected. (From Table II, $1/T^{*2}=T_c^2/T_i^2 \approx 5\times10^{-3}$ even for Cs halides for $T_i\approx1$°K.) At $T_i\approx1$°K therefore, using readily available magnetic fields, only the electronic entropy can be removed by isothermal magnetization and that in general only partially. If, however, one assumes that at T_i the magnetization produces an entropy change per F-center of $k\ln2$ (this would require fields of about 40 to 50 kilogauss), then from our evaluations given in Table I and Fig. 1, it is found that subsequent adiabatic demagnetization would produce temperatures, T_f^*, of about 3.

At this value of T_f^*, the specific heat per mole of F-centers would be 1.6 cal/mole-deg. In order to reach the more favorable region of large specific heat, where $T_f^*\approx1$, initial temperatures T_i^* about equal to 2 would be necessary.