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## COMMENTS AND ADDENDA

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# Spin-Lattice Relaxation near the Superconducting Transition: A Detailed Analysis for $V_3$Pt

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A detailed study has been made of the spin-lattice relaxation of the $V^{51}$ nucleus in $V_3$Pt for temperatures just above the superconducting transition. The quantity $1/T_1T$ is found to remain constant down to $T_c$ and has an average value $1/T_1T = 1.76 \pm 0.09$ (K sec)$^{-1}$.

We have measured spin-lattice relaxation times ($T_1$) of the $V^{51}$ resonance in the intermetallic compound $V_3$Pt at temperatures ($T$) from 1.2 to 4.2 K and at applied magnetic fields ($H$) between 4.5 and 12 kOe. This study was occasioned by a previous survey of relaxation properties in the $V_3X$ compounds,[1] in which measurements at $H = 9$ kOe appeared to indicate an increase in the quantity $1/T_1T$ just above the superconducting transition temperature ($T_c$) for the materials $V_3$Pt, $V_3$Ge, and $V_3$Si. The magnitude of the increases, approximately 10% for $V_3$Pt and $V_3$Ge and 20% for $V_3$Si, equalled or exceeded the experimental error (± 5%) in the data and, at the time of the investigation, the reason for such an increase was not understood. An observed structural transformation in $V_3$Si for $T \gtrsim T_c$[2] was suggested as a possible source for the enhanced relaxation rate. However, the resulting changes in electronic state densities expected on the basis of a rigid-band model of $V_3$Si[3] are not sufficiently large to account for a 10% change in $1/T_1T$,[4] and ultrasonic investigations[5] in $V_3$Ge and $Nb_3$Ge indicate no softening of the elastic constants analogous to that observed in $V_3$Si and other high-$T_c$ members of the $V_3X$ and $Nb_3X$ series. The fact that the increase was associated in each case with the superconducting transition temperature might suggest that it was related to some precursor effect of the superconducting transition. This is a particularly interesting possibility since the 3$d$ electrons in these compounds exhibit a strong one-dimensional character.[6] Fluctuations above $T_c$ are known to significantly affect the resistivity[7] and magnetic susceptibility[8] of two-dimensional materials. Although an estimate of the magnitude of fluctuation contributions to the relaxation rate in a one-dimensional system is difficult to make, it appears that none of the usual relaxation mechanisms could account for increases of the order observed.[9] In light of this current uncertainty, we have undertaken a detailed study of one of these systems: the $V^{51}$ resonance in $V_3$Pt.

The previous data[1] on these materials were part of a survey of most of the members of the $V_3X$ system. Except for $V_3$Si, the $T_1$'s were measured at one value of the magnetic field and at fairly large temperature intervals. The errors cited in these measurements are ±5%, which represents an uncertainty corresponding to approximately one standard deviation. In addition to this numerical uncertainty, it is important to have some measure of the adequacy of the form chosen to characterize the magnetization recovery. We have therefore extended the previous investigation in two ways. First, we have determined the phase diagram of the superconductivity in $V_3$Pt as a function of $H$

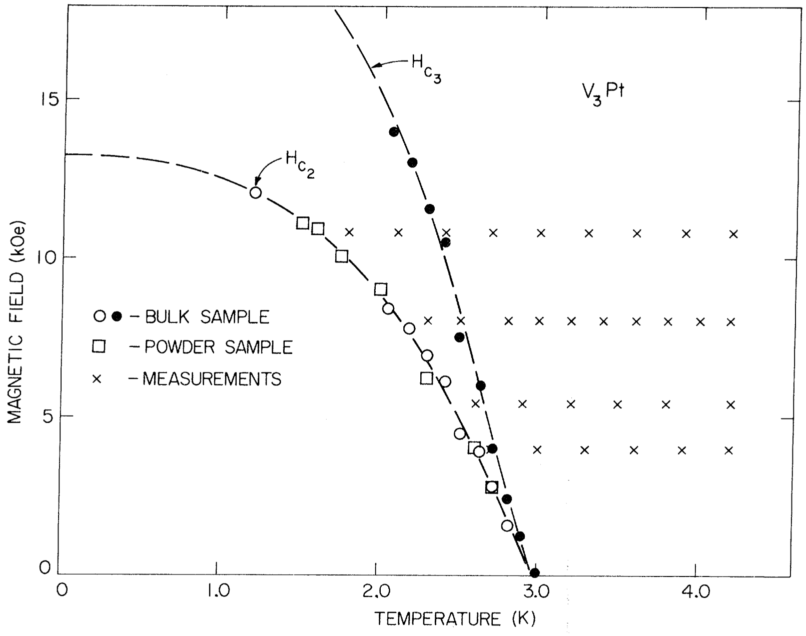

FIG. 1. Superconducting-normal phase diagram for $V_3Pt$. Values of the critical fields $H_{c2}$ and $H_{c3}$ are plotted as a function of temperature. Spin-lattice relaxation measurements were performed at each point on the figure indicated by a letter x.

and $T$ and have taken an extended series of $T_1$ measurements. Second, we have subjected the magnetization recovery data to a detailed least-squares fitting procedure,[10] which enables us to obtain quantitative information about the error involved as well as a statistical measure of the goodness of fit of the magnetization recovery to any assumed form. We have chosen the $V^{51}$ resonance in $V_3Pt$ for this study because the signal-to-noise ratio (~ 80:1 at 4.2 K) allows us to measure the magnetization recovery over a range of intensity of almost two decades. Its superconducting parameters [$T_c \simeq 2.9$ K, $H_{c2}(T=0) \simeq 13$ kOe] permit a detailed investigation of the entire range of critical fields with a conventional electromagnet at liquid-helium temperatures.

The superconducting properties of the sample were investigated by ac magnetization techniques[11] on both bulk and powdered samples of the material. At zero applied magnetic field, we find $T_c = 2.93 \pm 0.05$ K for the samples, in agreement with previous measurements.[12] The width of the transition is ± 0.01 K, and the error assigned here is associated with the vapor-pressure observations used to determine the temperature. The resulting values of the critical fields $H_{c2}$ and $H_{c3}$ are plotted as a function of temperature in Fig. 1. We find that the independent determinations of $H_{c2}$ and $H_{c3}$ result in a ratio of these two quantities, $H_{c3}/H_{c2}$, in extremely close agreement to the value 1.69 predicted theoretically.[13]

The $T_1$ measurements were performed at magnetic fields of 4.02, 5.36, 8.04, and 10.72 kOe. The actual temperature and field values of the observations are indicated on Fig. 1 by the letter x. There was no observed change of the resonance properties for field values such that $H_{c2} \leq H \leq H_{c3}$. Below $H_{c2}$, the magnetization recovery was observed to be nonexponential, which is presumably related to spatial variations of the energy gap in the sample.[14] Above $H_{c2}$, application of combs of saturating pulses or use of sweep saturation techniques yield exponential recoveries with an initial saturation value of ≥ 90%. Therefore, we choose to fit our recovery data to the form

$$M_z(t) = M_z(0) + [M_z(\infty) - M_z(0)](1 - e^{-t/T_1}) \ , \qquad (1)$$

where the equilibrium value of the nuclear magnetization $[M_z(\infty)]$, the magnetization immediately after saturation $[M_z(0)]$, and $T_1$ are taken as adjustable parameters. The values of $M_z(\infty)$, $M_z(0)$, and $T_1$ obtained from such a fitting procedure agree quite closely with those obtained by graphical techniques. The appropriateness of Eq. (1) was tested by performing a $\chi^2$ analysis. For the 12-MHz data, the mean value of $\chi^2$ for the fits at different $T$ values was 5.8 for ensembles of 20 data points, indicative of a very good fit. The resulting values of $1/T_1T$ are shown in Fig. 2, where the error flags represent a least-squares fit of $1/T_1$ to the data with a 90% confidence level. The mean value obtained from this fit for $1/T_1T$ is 1.76 $(\mathrm{K\,sec})^{-1}$, and the average uncertainty (as described above) is ± 5.6%. In terms of a customary standard deviation analysis, this error corresponds to ± 3.4%. The conclusion drawn from Fig. 2 is that, to within experimental accuracy, there is no evidence obtained from field or tem-

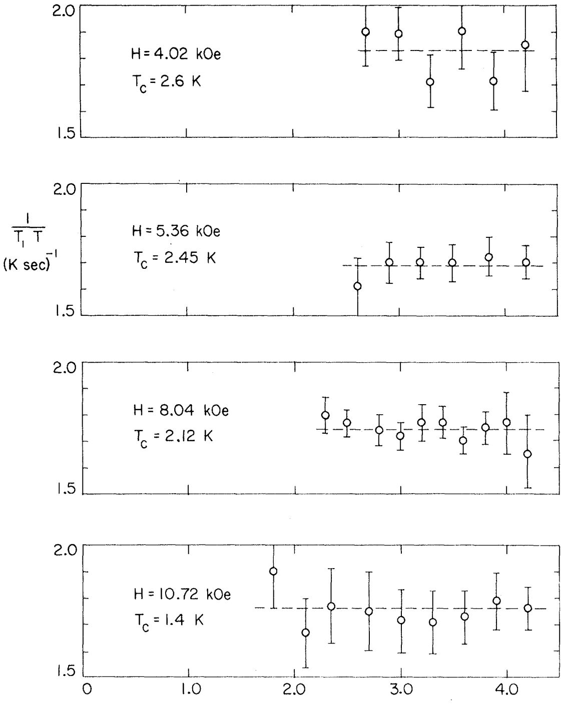

FIG. 2. Quantity $1/T_1T$ plotted as a function of temperature. To within the error discussed in the text, the data are observed to be independent of temperature with an average value of $1/T_1T = 1.76 \pm 0.09$ (K sec)$^{-1}$.

perature variation for nonconstancy of $1/T_1T$.[15]

On the basis of the experimental data, it is possible to assign an upper limit of ~ 3–5% to the possible magnitude of contributions to the relaxation rate in $V_3Pt$ resulting from fluctuations of the order parameter. There are uncertainties associated with any attempt to model the system theoretically. However, in addition to the calculation of $1/T_1$ for one- and two-dimensional fluctuations mentioned above,[9] a theoretical estimate of $1/T_1$ for a "dirty" bulk superconductor has been made.[16] The fluctuation contribution depends on the band structure and transport properties of the material and is directly proportional to the magnitude of $T_c$. Thus this effect might be expected to be stronger in superconductors with higher $T_c$'s. In $V_3Si$, the increase of $1/T_1T$ just above $T_c$ is approximately 20% and is clearly outside the range of experimental error. However, the presence of a structural transformation just above $T_c$ might also account for the increase in this case.[17] Recent measurements in $Nb_3Al$,[18] which has no similar transformation, do indicate a ~ 20% change in the value of $1/T_1T$ just above $T_c$. Whether this is a true effect of fluctuations of the superconducting order parameter is not yet known.

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[10] The fitting procedure used is based on "least-squares estimation of nonlinear parameters" by Donald W. Marquardt, IBM Share Library Distribution No. 309401 – NLIN 2, 1966 (unpublished).

[11] See, e.g., M. Strongin, A. Paskin, D. G. Schweitzer, O. F. Kemmerer, and P. P. Craig, Phys. Rev. Letters 12, 442 (1964); J. P. Burger, G. Deutscher, E. Guyon, and A. Martinet, Solid State Commun. 2, 101 (1964).

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[14] In $V_3Si$, for $T \ll T_c$ and $H \ll H_{c2}$, the magnetization recovery is observed to be exponential [B. G. Silbernagel, M. Weger, and J. H. Wernick, Phys. Rev. Letters 17, 384 (1966)]. We believe, however, that this form of the magnetization recovery occurs in a special case where the size of fluxoid cores is extremely small ($\xi \sim 25$ Å) relative to the lattice spacing ($d \sim 450$ Å). In $V_3Pt$ we have an intermediate case ($\xi \sim 125$ Å, $d \sim 450$ Å) which we will discuss in detail elsewhere.

[15] This result is consistent with Ref. 1, in the sense that the variation of $1/T_1T$ from 4.2 K [$= 1.94$ (K sec)$^{-1}$] to 2.8 K [$= 2.2$ (K sec)$^{-1}$] quoted there is approximately 13% and is comparable to the error limits. Another difference between the two sets of measurements is associated with the absolute magnitudes of $1/T_1T$ in this temperature region. The $V_3Pt$ data of Ref. 1 imply a value of $1/T_1T \simeq 2.05 \pm 0.1$ (K sec)$^{-1}$ while the present observations yield $1.76 \pm 0.09$ (K sec)$^{-1}$. The source of this 15% discrepancy (which is also comparable with the limits of error) is probably the different systematics of analysis employed.

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